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Description

Technical Field

5 The invention relates to dental compositions which can be used to make shaped dental articles, including prostheses, such as denture bases and denture liners, and restoratives by the controlled and gradual curing of the dental compositions via photoiniferter polymerization, the method of making the shaped dental articles via photoiniferter polymerization, and the shaped dental articles produced by the method.

10 Background of the Invention

Dentures are conventionally made from plastic materials. The tooth-holding portion of a denture is generally made from a rigid polymeric material of good dimensional stability and high impact strength. The gum portion frequently causes discomfort to the denture wearer. Consequently, much of the denture art has been concerned with providing comfort as well as a good fit to the denture wearer. Attempts have been made to alleviate denture wearer discomfort by providing denture liners made of soft elastomeric materials.

The most commonly used type of polymeric material from which denture bases and denture liners have been made is acrylic plastic. Many different types of acrylate polymers, copolymers, and crosslinked systems have been utilized for denture bases and denture liners. A detailed review of such materials is presented in Restorative Dental Materials, Seventh Edition (R. C. Craig ed.), C. V. Mosby Company, (1985), pp. 458-511. In general, the method of fabrication of such materials involves the free radical polymerization of acrylate monomers.

Most denture base plastics are prepared from powder-liquid compositions comprising poly(methyl methacrylate) beads, free radical polymerization initiator such as benzoyl peroxide, and monomer liquid consisting primarily of methyl methacrylate. Polymer beads comprising higher alkyl methacrylates, such as poly(ethyl methacrylate) and poly(butyl methacrylate), are typically used in the preparation of denture liners in order to provide flexibility to the denture liner. Lower acrylate beads are typically used in the preparation of denture bases. A method of making dental articles such as denture bases and denture liners involves mixing the appropriate polymerized beads and liquid monomer in order to form a mixture, packing the mixture in prepared flasks, followed by curing the mixture by the application of heat and pressure. Cold-curing systems which utilize amine accelerators are available, but, in general, provide acrylic polymers having inferior properties. Both the heat-curing process as well as the cold-curing process are labor intensive and require lengthy time periods of several hours.

In the dental fields of denture bases and denture liners, modifications to basic polymer systems have been made in an attempt to enhance the physical properties of the denture bases and the denture liners in order to provide both a good fit and comfort to the denture wearer. However, modifications to denture base materials and denture liner materials to meet these criteria have not met with complete success.

For example, U.S. Patent No. 4,300,886 describes a denture base made of a rigid polymethacrylate elastified by means of diamine lengthened polyurethane. However, such a modification compromises the physical properties of the denture base.

When both unmodified and modified denture base materials failed to provide the comfort sought after by the denture wearer, denture liners were fabricated to make the denture bases more comfortable. A variety of soft elastomeric materials were formulated for use in either combination with the denture base or in integral formation with the denture base, such as those compositions disclosed in U.S. Patent Nos. 3,339,283; 3,391,231; and 4,360,344. U.S. Patent Nos. 3,391,231 and 3,339,283 describe a method of fabricating an artificial denture by first molding a rigid denture base and then covering it with a hydraulic cushioning means formed from a cold cure silicone rubber.

U. S. Patent No. 4,360,344 describes a composite denture, wherein the tooth-holding portion is fabricated from a hard acrylic polymer and the mouth-engaging portion is fabricated from a soft non-hydrophilic polyurethane elastomer.

Each of the above polymers are prepared according to conventional free-radical polymerization processes. Thus, the processes once started and stopped provide materials of certain physical properties and shape which cannot be further modified without the inclusion of additional initiator. Thus, the above-described polymerization processes do not possess a "living" character.

55 The shaped dental articles prepared by the above-described methods are oftentimes uncomfortable for the dental patient and provide a poor fit. Dental articles also are difficult to fabricate utilizing the above-described methods.

A need therefore exists for denture bases and denture liners which are both comfortable and which provide

a good fit to the denture wearer. In addition, a need exists for denture bases and denture liners which are easy to fabricate. A need also exists for denture bases and denture liners which can be gradually cured by allowing the dental practitioner to start and stop the curing process at will.

Also used in dentistry, are restoratives based upon polymerizable diacrylates or dimethacrylates containing conventional free radical initiators. Such restoratives are discussed in the aforementioned reference entitled Restorative Dental Materials, pp. 225-252. The term "extraoral restorative" as used herein refers to a restorative made and cured outside the mouth which is subsequently placed inside the mouth. The term "direct restorative" as used herein refers to a restorative placed and cured directly in the mouth such as a tooth-colored composite restorative resin useful as a tooth-filling material.

The curing of known compositions used in forming restoratives occurs via a free radical chain reaction. Once terminated, the polymerization cannot be reinitiated simply by further light exposure and hence the customary practice is for the dental practitioner to first cure the restorative fully, and then use a dental tool, such as a bur, to cut back and shape the cured restorative to the desired anatomy. This is a time-consuming process for the dental practitioner and uncomfortable for the patient if the occlusion obtained is not correct.

The concept of light curing or cure on demand is currently gaining popularity in the field of dentistry. Recently a light activated denture base resin has been marketed under the tradename Triad[®] by Dentsply Corporation. The materials of this system consist of a prepolymerized polymethylmethacrylate embedded in a crosslinked network of a urethane dimethacrylate. These materials are discussed in an article by E.A. Lewis, R.E. Ogle, and S.E. Sorensen, Orthodontic Applications of a New Visible Light Curing Resin System, *NYS Dental Journal*, March, 1986, p. 32-34. Acrylate polymerizations, both chemical and light activated, are also used extensively in direct esthetic restoratives.

The aforementioned light activated systems represent classical free radical polymerizations. The molecular weight increases rapidly with time so that the extent of polymerization and crosslinking cannot be controlled by light exposure. Although the light curing aspect is an attractive feature of these systems, the properties of these materials are not as good as the heat cured materials. According to Clinical Research Associates (CRA) the best application of these materials appears to be for chair-side repairs and relining. (CRA Newsletter, Vol. 10(1), January 1986)

In all applications thus far in dentistry, the polymerization mechanism utilized has involved simple free radical kinetics. Thus, the molecular weight reaches its peak value very early during the polymerization and although extended time of reaction leads to greater conversion, this is not attendant with increased molecular weight. During the light activated polymerizations of dental materials known thus far, once the polymerization has been stopped by turning off the light source, it cannot be reinitiated by turning the light source back on.

A need therefore exists for direct and indirect restoratives, in addition to denture bases and denture liners, which can be cured gradually by allowing the dental practitioner to start and stop the curing process at will. Applicants have discovered a composition which employs iniferter technology.

The term "iniferter" or "photoiniferter" refers to a chemical compound that has a combined function of being a free radical initiator, transfer agent, and terminator, the term "iniferter" being a word formed by the underlined portions of the terms identifying these functions. The photo portion of the term indicates that the free radical polymerization is photolytically induced. This term and its use in the production of block copolymers is well known, particularly because of the work of Takayuki Otsu of the Department of Applied Chemistry, Osaka City University, Osaka, Japan. This work is discussed, for example, in an article by Otsu et al., entitled "Living Radical Polymerizations in Homogeneous Solution by Using Organic Sulfides as Photoiniferters", *Polymer Bulletin*, 7, 45-50 (1982) and an article by Otsu et al., entitled "Living Mono- and Biradical Polymerizations in Homogeneous System Synthesis of AB and ABA Type Block Copolymers", *Polymer Bulletin*, 11, 135-142 (1984) and European Patent Application No. 88303088.7, Publication date October 12, 1988, Publication Number 0.286.376. Despite the rather detailed description of making block copolymers according to such disclosures, there is no disclosure of dental compositions comprising acrylic photoiniferter block polymers and free radically polymerizable monomer which are suitable for the gradual and controlled formation of dental articles such as denture bases, denture liners, and restoratives.

The above references do not teach or suggest dental compositions comprising photoiniferter block polymer and free radically polymerizable monomer which can undergo stepwise polymerization to gradually increase the molecular weight and toughness of a dental article prepared therefrom upon controlled and intermittent exposure to ultraviolet or visible radiation by gradual polymerization and/or crosslinking.

Brief Description of the Invention

We have found a dental composition and a method of curing the dental composition in order to form shaped dental articles by a free-radical polymerization method which occurs in steps so that the extent of reaction.

molecular weight, and cross-linking can be controlled simply by turning a light source on and off. Thus, the polymerization mechanism is a "living polymerization", i.e. it can be reinitiated simply by turning a previously extinguished light source back on. This provides great latitude in controlling the extent of polymerization so that a partially cured dental article can be formed from the dental composition and shaped to a desired form or anatomy before final cure.

The dental composition of the present invention comprises reinforced acrylic photoiniferter block polymer, a monomer charge comprising free radically polymerizable monomer, and a filler. The reinforced acrylic photoiniferter block polymer possesses phase separated domains, thus offering flexibility along with toughness to dental articles formed from the dental composition. A photoiniferter is used as a means of promoting, controlling, and terminating polymerization of the photoiniferter block polymer. The photoiniferter block polymer is in turn used as a means of controlling and terminating polymerization of polymers of more advanced architecture useful as shaped dental articles by adding free radically polymerizable monomer to the photoiniferter block polymer in addition to a filler in order to form a dental composition.

The photoiniferter block polymer contained in the dental composition can undergo further polymerization by chain extension and/or crosslinking with the free radically polymerizable monomer with which it is combined in order to form a partially cured dental article. This is followed by the alternating steps of curing by intermittent exposure to actinic radiation (i.e., ultraviolet or visible radiation having a wavelength of 200 nm to 800 nm) and shaping of the article in order to form a final cured shaped dental article. This is accomplished without the use of additional polymerization initiators such as light activated initiators. The control of the polymerization in preparing the photoiniferter block polymer provided by the iniferter technology and the control of the polymerization and/or crosslinking in preparing the shaped dental articles from the dental composition comprising photoiniferter block polymer, free radically polymerizable monomer, and filler, permits the preparation of denture bases, denture liners and restorative compositions having controllable properties. By controlling the extent of cure, the physical nature of the material, i.e. its carvability and moldability, as well as its mechanical strength and toughness can be controlled. The generation of toughened thermosets by this technology provides shaped dental articles such as denture bases, denture liners, and restoratives of improved physical properties such as ultimate strength, fracture toughness, and wear over existing materials.

The terms "thermoset" and "thermosetting" as used herein refer to high polymers that solidify or "set" irreversibly when heated. This property is usually associated with a crosslinking reaction of the molecular constituents induced by heat or radiation.

The term "acrylic photoiniferter block polymer" as used herein refers to a homopolymer or block copolymer segment prepared by the photoiniferter polymerization of acrylic monomer which is useful in the dental composition of the present invention. The acrylic photoiniferter block polymer is capable of polymerizing free radically polymerizable monomer with which it is combined upon being subjected to a radiant energy source in order to form a shaped dental article.

A first aspect of the present invention relates to a dental composition comprising:
a mixture of

(i) an acrylic photoiniferter block polymer selected from $I(BT)_n$, $I(BAT)_n$, and mixtures thereof, wherein

I represents the free radical initiator portion of an iniferter of the formula $I(T)_n$;

T represents the terminator portion of the iniferter;

n is an integer of 1 to 12;

B represents an acrylic polymer block of suitable molecular weight;

A represents a normally thermoplastic polymer block having a glass transition temperature of at least 30°C;

(ii) a monomer charge comprising free radically polymerizable monomer of the formula $C(D)_x$ wherein

x is an integer ranging from 1 to 9;

D is an ethylenically unsaturated monovalent moiety; and

C is an organic residue; and

(iii) 5 to 90 weight % of a filler based upon the weight of said mixture;

wherein the weight ratio of the acrylic photoiniferter block polymer to the free radically polymerizable monomer of the formula $C(D)_x$ ranges from 1:99 to 99:1, and wherein controlled and intermittent exposure of the mixture to a radiant energy source capable of emitting radiation in a range of from 200 to 800 nm results in the partial polymerization or crosslinking of the acrylic photoiniferter block polymer and free radically polymerizable monomer to form a partially cured dental article capable of being shaped, after which a final exposure to the energy source provides a final cured dental article.

A second aspect of the present invention relates to a method of making a dental article comprising the steps of:

(i) forming a mixture of

(a) acrylic photoiniferter block polymer selected from $I(BT)_n$, $I(BAT)_n$, and mixtures thereof, wherein
 I represents the free radical initiator portion of an iniferter of the formula $I(T)_n$;
 T represents the terminator portion of said iniferter;
 n is an integer of 1 to 12;
 B represents an acrylic polymer block of suitable molecular weight; and
 A represents a normally thermoplastic polymer block having a glass transition temperature of at least 30°C;

(b) a monomer charge comprising free radically polymerizable monomer of the formula $C(D)_x$ wherein
 x is an integer ranging from 1 to 9;
 D is an ethylenically unsaturated group; and
 C is an organic residue; and

(c) 5 to 90 weight % of a filler based upon the weight of said mixture;
 wherein the weight ratio of the acrylic photoiniferter block polymer to free radically polymerizable monomer of the formula $C(D)_x$ ranges from 1:99 to 99:1;

(ii) exposing the mixture to radiation of 200 to 800 nm from a radiant energy source until polymerization or crosslinking of the acrylic photoiniferter block polymer and free radically polymerizable monomer occurs in order to form a partially cured dental article;

(iii) shaping the partially cured dental article of step (ii) as desired;

(iv) repeating steps (ii) and (iii) if necessary until the desired shape of the partially cured dental article has been obtained; and

(v) exposing the partially cured dental article of either step (iii) or step (iv) to a final exposure of radiation in order to form a final cured dental article.

A third aspect of the invention relates to shaped dental articles formed according to the method of the invention. The term "shaped dental article" as used herein refers to prostheses such as denture bases and denture liners, direct restoratives, and extraoral restoratives.

The shaped dental articles comprise as part of their polymer matrix cured reinforcing acrylic block copolymers. The use of "living" photoiniferter polymerization permits the interruption of the polymerization and/or crosslinking of the photoiniferter block polymer and $C(D)_x$ monomer at any time at which an intermediate or final desired physical consistency of the dental article has been attained. This enables polymerization of an initially fluid dental composition to intermediate putty stages at which it can be shaped, molded, cast, or carved to desired specifications and then finally cured to a hard set upon further exposure to radiation. For example, a dental practitioner may wish to terminate the curing process for a period of time in order to check the dental article such as a denture base, a denture liner or an extraoral restorative such as a tooth filling for proper fit. In the case of a direct restorative (i.e., a restorative placed and cured directly in the mouth), the dental practitioner may wish to terminate the curing process for a period of time in order to check the bite and carve in the required anatomy. By additional exposure to a radiant energy source the polymerization process may then be continued to provide the final shape to the dental article.

Thus, the use of the dental composition and method of the present invention results in a very substantial time savings for the dental practitioner and greatly increases the ease with which shaped dental articles can be fabricated. Additionally, the use of the shaped dental articles of the present invention results in a dramatic increase in comfort and a superior fit for the dental patient.

Detailed Description of the Invention

I. Dental Composition of the Present Invention and Preparation Thereof

The dental composition of the invention comprises acrylic photoiniferter block polymer combined with a monomer charge comprising free radically polymerizable monomer of the formula $C(D)_x$ and a suitable filler.

I.A. Photoiniferter Block Polymer

The first step in preparing the dental composition of the present invention involves the preparation of photoiniferter block polymer by using a photoiniferter compound in order to free radically polymerize one or two free radically polymerizable monomer charges in order to form photoiniferter block polymer of the formula $I(BT)_n$ or $I(BAT)_n$, respectively.

A monomer charge comprising free radically polymerizable acrylic monomer is dissolved in a suitable inert solvent, if needed, and polymerized by a first free radical polymerization utilizing a suitable iniferter of the formula $I(T)_n$ as a free radical initiator source in order to form a photoiniferter block polymer of the formula $I(BT)_n$.

Generally, from 0.01 to 5 percent by weight of iniferter based upon the total weight of polymerizable composition is used.

The iniferter is caused to dissociate to form free radicals $I(\cdot)_n$ and $nT\cdot$ by exposure to an appropriate energy source. The preferred iniferter is one which will dissociate upon exposure to a radiant energy source, such as an ultraviolet or visible light source, preferably an ultraviolet radiant energy source. Upon exposure to the energy source, the iniferter dissociates to form free radicals which promote free radical polymerization of acrylic monomer of the first monomer charge. Upon completion of the free radical polymerization of the free radically polymerizable acrylic monomer to form free radical polymer segment $I(B\cdot)_n$, the energy source is discontinued to permit the free radically polymerized segment $I(B\cdot)_n$ to recombine with the terminator portion $nT\cdot$ of the iniferter to form photoiniferter block polymer of the formula $I(BT)_n$.

In order to prepare the photoiniferter block copolymer of formula $I(BAT)_n$, a second monomer charge comprising free radically polymerizable acrylic monomer is combined with the photoiniferter block polymer $I(BT)_n$ in order to form a second mixture. The second mixture is exposed to the energy source in order to cause dissociation of $I(BT)_n$ to form free radicals $I(B\cdot)_n$ and $nT\cdot$ and the free radical polymerization of the second monomer charge onto the first polymer segment $I(B\cdot)_n$, that now being the initiator of the second free radical polymerization. Upon completion of polymerization of the second monomer charge, exposure to the energy source is terminated and the terminator portion $nT\cdot$ of the iniferter combines with $I(BA\cdot)_n$ to form photoiniferter block polymer of the formula $I(BAT)_n$.

The particular energy source and its intensity are selected to result in the dissociation of the photoiniferter to form free radicals. When employing a photoiniferter which will dissociate upon exposure to ultraviolet light radiation, an ultraviolet light source is utilized. When employing a photoiniferter which will dissociate upon exposure to visible light radiation, a visible light source is utilized. The intensity or rate of radiation is chosen such that it will advance the polymerization at a reasonable rate without deleteriously affecting the polymer segment being produced. A light source having a wavelength 200 to 800 nm, preferably 300 to 400 nm, spaced approximately 10 cm from the reaction vessel, to provide an exposure of 2 milliwatts per square centimeter has been found to produce suitable results.

Reaction times on the order of 2 to 50 hours in the absence of a metal compound accelerator have been found to be typical, depending upon the intensity of the radiation, with faster reaction times being observed at greater intensities. Reaction times in the presence of a metal compound accelerator have been found to be 0.2 to 5 hours.

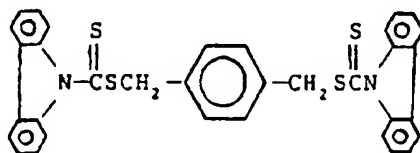
The reactions involving the preparation of the photoiniferter block polymers $I(BT)_n$ and $I(BAT)_n$ are preferably conducted in a vessel with agitation to permit uniform exposure of the reactants to the energy source. While most of the reactions involving the preparation of photoiniferter block polymers have been conducted by employing a batch process, it is possible to utilize the same technology in a continuous polymerization operation.

Photoiniferter block polymer selected from $I(BT)_n$, $I(BAT)_n$, and mixtures thereof, the preparation of which is described above, is subsequently mixed with a monomer charge comprising free radically polymerizable monomer of the formula $C(D)_x$ in order to provide the dental composition of the present invention which can be cured in stages in order to provide a shaped dental article.

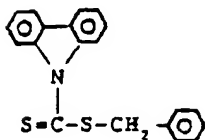
I.A.(i) Photoiniters

Photoiniters useful in forming the photoiniferter block polymer useful in the dental compositions of the present invention are those of the general formula $I(T)_n$, wherein I represents the free radical initiator portion of an iniferter of the formula $I(T)_n$, T represents the terminator portion of said iniferter, and n is an integer of 1 to 12.

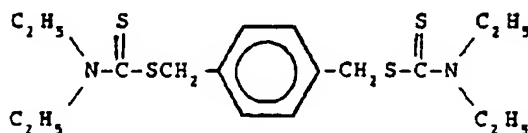
The preferred photoiniters for use in producing the photoiniferter block polymers useful in the dental compositions of the invention are those represented by the formulae:



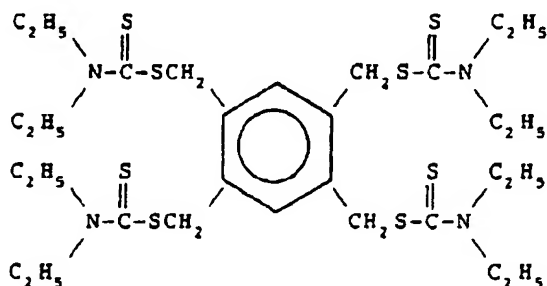
xylene carbazoyldithiocarbamate [XCDC];



benzyl carbazolythiocarbamate [CDC] (monofunctional photoiniferter);



xylene bis(N,N-diethyldithiocarbamate) [XDC] difunctional photoiniferter;



durene $\alpha, \alpha', \alpha'', \alpha'''$ -tetrakis(N,N-diethyldithiocarbamate) [DDC] (tetrafunctional photoiniferter); and mixtures thereof.

I.A. (II) Polymer Block B

Polymer block B of the photoiniferter block polymer of the formula I(BT)_n or I(BAT)_n, comprises an acrylic polymer block of suitable molecular weight. Polymer block B should have a suitable molecular weight such that the shaped dental article formed from the dental composition possesses the desired mechanical properties. Typically, the molecular weight of the polymer block B for I(BT)_n or I(BAT)_n ranges from 1000 to 50,000. Preferably, the monomer used in forming polymer block B is monofunctional in order to avoid crosslinking. Monomers useful in forming polymer block B include but are not limited to those selected from acrylic acid; methacrylic acid; esters of acrylic acid and alcohol wherein the alcohol comprises from 1 to 22 carbon atoms; esters of methacrylic acid and alcohol wherein the alcohol comprises from 1 to 22 carbon atoms; and mixtures thereof. Examples of such esters include methyl methacrylate, isobornyl methacrylate, phenethyl methacrylate, isopropyl methacrylate, n-propyl methacrylate, n-butyl acrylate, ethyl acrylate, 2-ethyl-hexyl acrylate, isobutyl acrylate, methyl acrylate, n-propyl acrylate, iso-octyl acrylate, and the like. Optionally, one or more non-interfering oxygen, nitrogen, sulfur, fluorine, and phosphorous containing functionalities can be present on the monomers useful in forming polymer block B.

The preferred monomers for use in forming polymer block B include methyl methacrylate, isobornyl methacrylate, phenethyl methacrylate, n-butyl acrylate, ethyl acrylate, iso-octyl acrylate, and mixtures thereof. Optionally, one or more non-interfering oxygen, nitrogen, sulfur, fluorine, and phosphorus containing functionalities can be present on such monomers.

For photoiniferter block polymers of the formula I(BT)_n, polymer block B preferably has a glass transition temperature ranging from -200°C to 400°C. For photoiniferter block polymers of the formula I(BAT)_n, polymer block B preferably has a glass transition temperature ranging from -200°C to 100°C. In addition, the glass transition temperature of polymer block B is preferably at least about 50°C lower than the glass transition temperature of polymer block A for I(BAT)_n in order to obtain shaped dental articles having a range of properties.

I.A.(iii) Polymer Block A

Polymer block A of the photoiniferter block polymer I(BAT)_n comprises a normally thermoplastic polymer block having a glass transition temperature (T_g) of at least 30°C. Preferably, the monomer used in forming polymer block A is monofunctional in order to avoid crosslinking. Preferably, the T_g of polymer block A is about 50°C higher than the T_g of polymer block B for the photoiniferter block polymer I(BAT)_n. Preferably, polymer block A has a glass transition temperature ranging from 30°C to 150°C and polymer block B has a glass transition temperature ranging from -200°C to 100°C for photoiniferter block polymer I(BAT)_n.

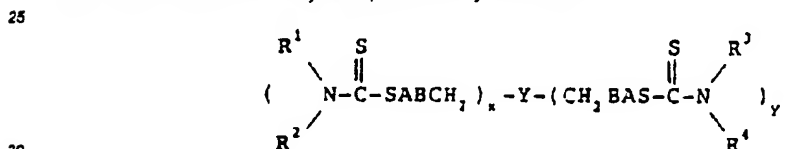
Monomers useful in forming polymer block A include but are not limited to methyl methacrylate, phenethyl methacrylate, isobornyl methacrylate, isopropyl methacrylate, n-propyl methacrylate, and mixtures thereof. The preferred monomers for use in forming polymer block A are selected from the group consisting of methyl methacrylate, isobornyl methacrylate, phenethyl methacrylate, and mixtures thereof.

I.A.(iv) Preferred Photoiniferter Block Polymers

The preferred photoiniferter block polymers for use in the dental composition of the present invention are those wherein n is an integer ranging from 2 to 12 for I(BAT)_n, and 1 to 8 for I(BT)_n. Most preferably in ranges from 2 to 6 for I(BAT)_n.

For I(BAT)_n, the preferred weight ratio of polymer block B to polymer block A ranges from 95:5 to 5:95. Most preferably, the weight ratio of polymer block B to polymer block A ranges from 20:80 to 80:20 in order for phase separation and toughening to occur.

The preferred photoiniferter block polymers of the formula I(BAT)_n for use according to the present invention include those which may be represented by the formula



wherein

R¹, R², R³ and R⁴ are aliphatic, aromatic, or substituted aromatic moieties, which can be the same or different and which do not substantially interfere with the ability of I· to promote free radical polymerization or with T· to recombine with I· or a polymer free radical segment including I·;

Y is a linking group having a functionality of x+y which does not substantially interfere with the ability of I· to promote free radical polymerization or the ability of T· to recombine with I· or a polymer free radical segment including I·; and

x and y are each integers of at least 1 and the sum of x+y is not more than 12.

Preferably R¹, R², R³, and R⁴ which can independently be the same or different are selected from C₁₋₄ aliphatic moieties. An example of a suitable linking group Y is



The selection of the photoiniferter block polymer for inclusion in the dental composition of the present invention depends upon the ultimate application of the dental composition. When a shaped dental article possessing greater flexibility and toughness is desired, the photoiniferter block polymer I(BAT)_n, wherein n is an integer greater than 2, is preferably included in the dental composition.

I(BT)_n and subsequently I(BAT)_n can be made by a method having the following steps. An iniferter represented by the general formula I(T)_n capable upon being subjected to an appropriate energy source of forming free radicals I(·)_n and nT· wherein I· is a highly reactive free radical capable of initiating free radical polymerization, and T· is a less reactive free radical which is generally much less capable of initiating free radical polymerization than I· but will rejoin with I(·)_n or a free radical polymer segment free radically polymerized with I(·)_n upon termination of said energy source is mixed with a first monomer charge consisting of acrylic monomer polymerizable to form an acrylic polymer block wherein the monomer is free radically polymerizable in the pres-

ence of $I(\cdot)_n$ to form a first polymer block. The mixture is exposed to an energy source capable of forming free radicals $I(\cdot)_n$ and $nT\cdot$. The exposure is maintained until the first monomer charge polymerizes with $I(\cdot)_n$ to form a free radical polymer segment represented by the formula $I(B\cdot)_n$, wherein B represents the first polymer block formed of the first monomer charge. Exposure is terminated whereby to cause $I(B\cdot)_n$ and $nT\cdot$ to combine to form a polymer represented by the formula $I(BT)_n$.

$I(BT)_n$ can be mixed with a second monomer charge which is free radically polymerizable in the presence of $I(B\cdot)_n$ to a second polymer block. $I(BT)_n$ is exposed to an energy source capable of forming free radicals $I(B\cdot)_n$ and $nT\cdot$. The exposure is maintained until the second monomer charge polymerizes with $I(B\cdot)_n$ to form a free radical block copolymer segment represented by the formula $I(BA\cdot)_n$, wherein A represents the second polymer block formed of the second monomer charge. Exposure is terminated whereby $I(BA\cdot)_n$ and $nT\cdot$ combine to form a block copolymer represented by the formula $I(BAT)_n$.

Preferably, photoiniferter block polymer of the formula $I(BT)_n$ or $I(BAT)_n$ is used in the dental composition of the present invention rather than a combination of $I(BT)_n$ and $I(BAT)_n$ for practical considerations.

A person skilled in the area of dental products will recognize that by the judicious selection of dental composition components one can prepare dental compositions useful in forming dental bases, denture liners, and dental restoratives such as direct restoratives and extraoral restoratives.

I.B. Free-Radically Polymerizable Monomer of the Formula $C(D)_x$

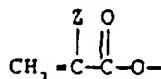
A monomer charge comprising free radically polymerizable monomer is combined with the photoiniferter block polymer in order to form the dental composition of the present invention. The free radically polymerizable monomer included in the dental composition has the general formula $C(D)_x$, wherein

x is an integer of 1 to 9;

D is an ethylenically unsaturated monovalent moiety; and

C is an organic residue.

D can comprise an ethylenically unsaturated monovalent moiety including but not limited to those of the following general formula



wherein

Z is selected from the group consisting of hydrogen, halogen, C_{1-8} alkyl, and C_{7-12} aryl alkyl. Preferably, D comprises the above structure wherein Z is selected from -H and $-\text{CH}_3$ for reasons of increased rate of polymerization. Most preferably, D comprises the above structure wherein Z comprises $-\text{CH}_3$ for reasons of reduced toxicity in addition to increased rate of polymerization.

C has been defined as an organic residue. Preferably the organic residue C comprises an alkyl group comprising from 1 to 30 carbon atoms. Optionally, non-interfering oxygen, nitrogen, sulfur, phosphorus, and fluorine containing functionalities can be present in the alkyl residue. Useful organic residues are those that provide an optional balance of such factors as strength, durability, opacity or translucency, toxicity or irritancy, etc. For example, if a more rigid shaped dental article is desired C preferably comprises 1 to 18 carbon atoms. More preferably, for a rigid shaped dental article, C comprises a hydrocarbyl residue comprising 1 to 18 carbon atoms and 1 to 10 noninterfering oxygen, sulfur or nitrogen atoms. Most preferably, for a rigid shaped dental article, C comprises 1 to 18 carbon atoms and 1 to 8 noninterfering oxygen, sulfur or nitrogen atoms.

Refractive indices of the dental compositions of the present invention should range from 1.30 to 1.70 prior to the addition of additives such as fillers or pigments, preferably from 1.35 to 1.65, and most preferably from 1.40 to 1.60.

Examples of suitable $C(D)_x$ monomers include but are not limited to alkyl, aryl, and aralkyl monoacrylates and monomethacrylates which optionally include one or more non-interfering heteroatoms (e.g., butyl acrylate, phenethyl methacrylate, norbornyl acrylate, isobornyl methacrylate, diglycidyl methacrylate); alkyl, aryl, and aralkyl diacrylates and dimethacrylates of diethylene glycol, triethylene glycol, 2,2-dimethylpropane diol, tetraethylene glycol, and hexane diol which optionally include one or more non-interfering heteroatoms (e.g. diethylene glycol diacrylate, diethylene glycol dimethacrylate, triethylene glycol diacrylate, triethylene glycol dimethacrylate, 2,2-dimethylpropane diol diacrylate, 2,2-dimethyl propane diol dimethacrylate, tetraethylene glycol diacrylate, tetraethylene glycol dimethacrylate, hexane diol diacrylate, hexane diol dimethacrylate,

ethoxylated bisphenol A diacrylate, ethoxylated bisphenol A dimethacrylate [commonly known as BIS-GMA]; and alkyl, aryl, and aralkyl multifunctional acrylates and methacrylates which optionally include one or more non-interfering heteroatoms, (e.g., pentaerythritol trimethacrylates, pentaerythritol tetramethacrylates), and mixtures thereof.

The selection of free radically polymerizable $C(D)_x$ monomer can be made to facilitate the addition of fillers or additives, if needed or desired, to form the appropriate dental compositions of the invention. This is accomplished by selecting $C(D)_x$ monomer or a mixture of $C(D)_x$ monomer possessing a viscosity of 10 to 500 cps and a refractive index of 1.30 to 1.70. The preferred range of viscosity for mixtures of $C(D)_x$ monomer ranges from 50 to 360 cps. The preferred refractive index of $C(D)_x$ monomer ranges from 1.40 to 1.60.

It is possible to provide a dental composition which will provide a cross-linked network upon cure. If a die-ethylenically unsaturated $C(D)_x$ compound (wherein x equals 2) or a multi-ethylenically unsaturated $C(D)_x$ monomer compound (wherein x is greater than 2) is used a segmented cross-linked network is formed. This will provide increased fracture toughening properties to the resultant shaped dental articles. Preferably, x is greater than 2 in order to facilitate crosslinking.

The ratio of the photoiniferter block polymer to the free radically polymerizable monomer of the formula $C(D)_x$ in the dental composition of the invention can range from 1:99 to 99:1, preferably from 10:90 to 90:10, and most preferably from 25:75 to 75:25.

1.C. Fillers

Filler particles for use in the dental compositions of the present invention include organic fillers, inorganic fillers and mixtures thereof which are suitable for use in the oral environment.

Examples of suitable inorganic fillers include but are not limited to diatomaceous or precipitated silica, powdered glass, powdered quartz, nitrides (e.g., silicon nitride), borosilicate glass, barium glass, hydroxyapatite, ceramic metal oxides (e.g., CaO , Sb_2O_3 , SnO_2 , ZrO_2 , BaO , Al_2O_3 and $CaCO_3$), submicron silica particles (e.g., pyrogenic silicas such as the Aerosil™ Series OX 50™, "130", "150" and "200" silicas sold by Degussa and Cab-O-Sil M5™ silica sold by Cabot Corp.), and mixtures thereof.

Examples of suitable organic filler particles include but are not limited to filled or unfilled pulverized polyacrylates or polymethacrylates [e.g., poly(methyl methacrylate)], polycarbonates, polyepoxides, mixtures thereof and the like. Preferred filler particles comprise quartz, submicron silica, and non-vitreous microparticles of the type described in U.S. Patent No. 4,503,169.

A "ceramic" metal oxide is an inorganic oxide which, when in its pure form, can be fired or sintered into a rigid or self-supporting polycrystalline form that is stable in a normal air environment, e.g., 23°C, and 50 percent relative humidity. Suitable ceramic metal oxides are non-toxic when incorporated into the microparticle and are colorless or only weakly colored, e.g., BaO , Bi_2O_3 , CaO , Nb_2O_5 , Sb_2O_3 , SnO_2 , Ta_2O_5 , TiO_2 , Y_2O_3 , ZnO , ZrO_2 , and oxides of the lanthanide series (e.g., CeO_2 , Ce_2O_3 and La_2O_3), as well as mixtures and mixed oxides thereof. Preferred ceramic metal oxides include HfO_2 , La_2O_3 , SrO , ZrO_2 , and mixtures thereof, with ZrO_2 being more preferred. Characteristically, substantially all (e.g., 90 weight percent or more) of the radiopacifying ceramic metal oxide in the microparticle is present in its polycrystalline form, and substantially none (e.g., 10 weight percent or less) is present in an amorphous form.

A preferred method for preparing the microparticles of the present invention, referred to herein as "sol-gel" method, involves the combining of (1) an aqueous or organic dispersion or sol of amorphous silica with (2) an aqueous or organic dispersion, sol, or solution of the desired radiopacifying ceramic metal oxide or a precursor organic or inorganic compound which is calcinable to the desired radiopacifying ceramic metal oxide. For brevity, the aforementioned dispersion or sol of silica will be sometimes referred to hereafter as the "silica starting material", and the aforementioned dispersion, sol, or solution of the radiopacifying ceramic metal oxide or precursor compound will sometimes be referred to hereafter as the "ceramic metal oxide starting material". The mixture of silica starting material and ceramic metal oxide starting material is dried to a solid, ground, fired, and reground to form microparticles of the invention. The microparticles can then be combined with an appropriate resin to form a composite.

Although either aqueous or organic silica starting materials can be employed in the sol-gel method, aqueous silica starting materials are preferred for reasons of economy. Suitable aqueous silica starting materials preferably contain colloidal silica at concentrations of 1 to 50 weight percent, more preferably 15 to 35 weight percent. Suitable organic silica starting material include organosols containing colloidal dispersions of silica in organic solvents (preferably water-miscible polar organic solvents) such as ethanol, normal or isopropyl alcohol, ethylene glycol, dimethylformamide and the various "Cellosolve" glycol ethers. The size of the colloidal silica particles in the silica starting material can vary, e.g., from 0.001 to 0.1 micrometers, preferably 0.002 to 0.05 micrometers.

Preferred silica starting materials which can be used in this invention include aquasols sold under the trademark "Ludox" from E.I. DuPont de Nemours and Co. Other useful silica starting materials include dispersions or aquasols sold under the trademarks "Nalco", "Syton" and "Nyacol". Additional suitable commercially available silica starting materials are listed in said U.S. Pat. Nos. 3,709,708 and 3,793,041.

Preferably, the silica starting material is filtered to remove extraneous solids, bacterial growth and other impurities. More preferably, the silica starting material is filtered through a microfine filter, as described in more detail below. If described, the silica can be modified by addition of other inorganic compounds, for example, those compounds (e.g., B_2O_3) which can form amorphous microregions under the conditions used to prepare the microparticles of the present invention. It should be borne in mind that the addition of such inorganic compounds may alter the refractive index of the final microparticles, and may effect the visual opacity of a dental composite prepared therewith.

Although either aqueous or organic ceramic metal oxide starting materials can be employed in the sol-gel method, aquasols are preferred for reasons of economy. Suitable commercially available ceramic metal oxide aquasols include CaO_2 , Sb_2O_5 , SnO_2 and ZrO_2 aquasols. Commercial ZrO_2 aquasols typically contain a small amount (e.g., 1 to 3 weight percent) of HfO_2 as a contaminant. Suitable calcinable precursor compounds preferably are carboxylates (e.g., acetates, formates, oxalates, lactates, propylates, citrates, or acetylacetonates) or salts of mineral acids (e.g., nitrates), selection of particular precursor compound being dictated by availability and ease of handling. Use of precursor compounds which might form precipitates or undesired crystalline microregions prior to gelation, or form water- or acid-soluble compounds or colored impurities in the microparticles, preferably should be avoided. Representative precursor compounds useful in the present invention include barium acetate, lanthanum nitrate, strontium nitrate, tantalum nitrate, and zirconium acetate.

Other metal oxides which may not themselves provide sufficient radiopacity can, if desired, be included in the microparticles of the present invention. Such other metal oxides can be useful, for example, to adjust various physical properties of the microparticles (e.g., refractive index, hardness, density or porosity) or physical properties of dental composites prepared therewith (e.g., viscosity before cure, or compressive strength, tensile strength, or visual opacity after cure). Such other metal oxides include Al_2O_3 and CaO . When the above-described sol-gel method of preparation is employed, such other metal oxides can be introduced into the final microparticles by combining a dispersion or sol containing the desired other metal oxide (or a suitable dispersion or sol containing a precursor compound calcinable thereto) with the silica starting material and ceramic metal oxide starting material. If desired, such other metal oxides can be introduced by using a silica sol containing silica particles coated with such other metal oxide (e.g., "Nalco" 612 or 613 alumina-coated silica aquasols).

In a most preferred embodiment, the sol-gel method is carried out as follows. First, an aquasol containing colloidal silica is mixed with a rapidly stirred sol or solution containing the desired radiopacifying ceramic metal oxide (e.g., ZrO_2) or calcinable precursor compound (e.g., zirconium acetate). For some starting materials, reverse order of addition can lead to non-uniform interspersal of the amorphous and crystalline microregions in the final microparticle. The mixture preferably should be sufficiently acidic to prevent non-uniform gelation from occurring. For example, the pH preferably is below 4.5 for a silica:zirconium acetate mixture. The mixture is then gelled, e.g., by raising the pH, by dehydration (using, for example, a "Rotovap" apparatus), or by heating the mixture at a temperature below its boiling point. For example, dehydration by heating below $75^\circ C$. can be used for a silica:zirconium acetate mixture.

The gel may contain a significant portion of the water or other solvents present in the starting materials. The gel is heated at a temperature and pressure sufficient to remove the water or solvents without causing boiling of the gel, e.g., for 20-24 hours at $75^\circ C$. and ambient pressure, thereby yielding a dried or substantially dried solid. Drying preferably is carried out in shallow pans. The dried solid breaks up into small granules. The small granules preferably are pulverized or comminuted to facilitate removal of organic compounds. The granules are then heated at a temperature and pressure sufficient to remove substantially all such organic compounds, e.g., in air at atmospheric pressure for 2-4 hours at 200° - $600^\circ C$. preferably 300° - $600^\circ C$. Differential thermal analysis or gravimetric analysis can be used to determine the extent of organic compound removal. The resulting powder is very friable and can be further pulverized.

The powder is next fired at a temperature and for time sufficient to convert the ceramic metal oxide or precursor to polycrystalline ceramic metal oxide. The firing time and temperature should not be excessive, as it is desirable to retain oxide of silicon in its amorphous state, prevent the growth or formation of crystalline microregions having diameters greater than 0.4 micrometers, and densify the microparticles to reduce the incidence of voids. During the firing cycle, the microparticles will undergo significant changes in density, surface area, pore volume and pore size. Density tends to increase during firing, while surface area and pore volume tend to decrease. For example, in 5.5:1 mole ratio SiO_2 : ZrO_2 microparticles, density reaches about 2.50 gm/cc after firing to about $1000^\circ C$. Surface area reaches a maximum after firing to $400^\circ C$. (at a value of about 175-

200 m²/g as measured by the BET method), declines after firing to 950°C. (to a value of about 50-75 m²/g), then declines further after firing to 1000°C (to a value of about 4-6 m²/g). Average pore volume reaches about 40% of the microparticles (as determined using the BET method) after firing at 400°-700°C., then drops to substantially zero after firing to about 1000°C. For SiO₂:ZrO₂ microparticles, firing should be carried out to an extent sufficient to form polycrystalline zirconia (e.g., tetragonal ZrO₂), while avoiding formation of zircon (ZrSiO₄) or cristobalite (SiO₂) crystalline microregions. Firing temperatures between 1000° and 1100°C., are preferred.

The term "green state milling" will be used herein to describe milling of the microparticles before the ceramic metal oxide has been fired to its polycrystalline form. Use of green state milling has been found to be very beneficial in obtaining dental composites with good cure stability, particularly when both green state milling and optimization of firing temperatures is employed.

To predict cure stability for dental composites prepared from SiO₂:ZrO₂ microparticles, it has been found useful to evaluate the pH of the microparticles after firing by contacting an aqueous slurry of the microparticles with alizarin indicator. SiO₂:ZrO₂ microparticles which causes the indicator to turn yellow (pH<8) tend to form dental composites with better cure stability than SiO₂:ZrO₂ microparticles which cause the indicator to turn pink-red (pH<7). The aforementioned green state milling step has been found useful for making SiO₂:ZrO₂ microparticles which cause alizarin indicator to turn yellow.

In addition to the factors already noted above, higher firing temperatures tend to increase the hardness of the microparticles and decrease water absorption. Higher firing temperatures typically also lead to faster polymerization set times for dental composites prepared from the fired microparticles.

Firing can be carried out, for example, in a muffle furnace, with the dried powder contained in a shallow layer (e.g., 25 mm deep) in a vitreous silica boat. The fired product is then reground to provide microparticles having the desired average particle diameter, e.g., less than 50 micrometers. Regrinding can be carried out using conventional equipment and preferably employs grinding media having the same refractive index as the microparticles.

The relative molar ratio or oxide of silicon to ceramic metal oxide in the microparticles should be adjusted to provide the desired refractive index and degree of radiopacity. For the most preferred SiO₂:ZrO₂ microparticles, the molar ratio of SiO₂ to ZrO₂ desirably is 2:1 or more, with values between 3:1 and 9:1 being preferred, and values between 5:1 and 7.5:1 being most preferred. For microparticles containing other silica:ceramic metal oxide mixtures, the ratio of silica to ceramic metal oxide should be adjusted to provide the desired degree of radiopacity coincident with attainment of the desired refractive index and other desired physical properties in the microparticles and attainment of the desired visual opacity, durability, cure stability, and other desired physical properties in dental composites prepared therewith.

The relative ratio of oxide of silicon to ceramic metal oxide can also influence polymerization set time rates for dental composites prepared therewith, with higher oxide of silicon content typically leading to faster set times.

It is particularly desirable to avoid formation within the microparticles of crystalline microregions or inhomogeneities (e.g., voids) having diameters greater than 0.4 micrometers, a dimension which corresponds to the shortest wavelength of visible light. The presence in the microparticles of such crystalline microregions or inhomogeneities will undesirably increase the visual opacity of a dental composite prepared therewith. Thus, the microparticles of the present invention are formulated under condition that substantially discourage or prevent the formation of such crystalline microregions and inhomogeneities. For brevity, such crystalline microregions and inhomogeneities will sometimes be referred to hereafter as "visually opacifying inclusions."

Prevention of visually opacifying inclusions can be achieved by filtering the silica starting material and/or ceramic metal oxide starting material through a microfine filter having a pore diameter less than 0.4 micrometers. A preferred filtration technique employs a series of progressively finer "Ballston" filters with the last filter in the series having a pore diameter less than 0.2 to 0.25 micrometers. During subsequent processing, the gel formed by combination of the starting materials should be kept free of contaminants. During firing of the dried and ground solid obtained from the gel, care should be taken to avoid firing temperatures and times which might promote growth of crystalline microregions to an extent sufficient to form visually opacifying inclusions, or promote reaction between the various inorganic species within the microparticles and formation of new crystalline microregions containing visually opacifying inclusions. In general, firing temperatures above about 1100°C. tend to promote formation of visually opacifying inclusion (usually as enlarged or new crystalline microregions, or as voids or cracks) and thus should be avoided.

It is preferable to treat the surface of the filler particles with a coupling agent in order to enhance the bond between the filler and the organic polymer matrix. The use of such coupling agents is well known in the art. Examples of suitable coupling agents include gamma-methacryloxy-propyltrimethoxy silane, gamma-mercaptopropyltriethoxy silane, gamma-aminopropyltrimethoxy silane and the like.

Other types of useful fillers include inorganic-filled organic fillers such as those described in UK Patent No. 1,278,413, Publication Date June 21, 1972. Useful filler particles can be either radiopaque or non-radiopaque depending upon the particular application. For dental compositions useful in forming denture bases and denture liners non-radiopaque fillers are acceptable. For dental compositions useful in forming restoratives, a radiopaque filler is preferred. About 5 to 90 weight percent of a filler is included in the dental composition of the present invention, preferably 40 to 80 weight percent.

It is within the scope of this invention to include various other components in the dental composition formulations useful in forming denture base, denture liners, and dental restoratives. For example, it may be desirable to include such materials as colorants (e.g. pigments and/or dyes), stabilizers, sensitizers, metal compound accelerators, medicaments, and/or various polymeric additives. These materials are typically added to the dental composition prior to the exposure of the dental composition to the radiant energy source.

Metal Compound Accelerators

One or more metal compound accelerators may be added to the dental compositions of the invention to enhance the rate of polymerization of the photoiniferter block polymer and C(D)x monomer, thus speeding up the cure time. One or more metal compound accelerators may also be used in the initial preparation of the photoiniferter block polymer which is contained in the dental composition.

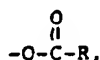
Thus, a polymerization accelerating amount of at least one metal compound which is capable of accelerating free radical polymerization may be added such that it is present during the polymerization of at least one monomer charge during the synthesis of the photoiniferter block polymer. In addition, a polymerization accelerating amount of at least one metal compound which is capable of accelerating free radical polymerization may be added to the dental composition of the present invention such that it is present during the preparation of the shaped dental article. The metal compound should not interact with the free radically polymerizable monomer to which it is added in order to form an insoluble compound in an amount which would substantially interfere with the polymerization or crosslinking reactions.

Preferably, the metal compound is represented by the general formula $M_z L_x$ wherein

M is a cation having a valency of z of a metal which is selected from the group consisting of tin, zinc, cobalt, titanium, lead, and palladium;

x is an integer of at least 1;

L is an anion having a valency of x which is selected from C₁₋₂₀ alkyl, aryl, -OR,



NO₃⁻, SO₄²⁻, and PO₄³⁻;

R is selected from C₁₋₂₀ alkyl and aryl; and

z is an integer of at least 1.

Most preferably, the metal compound is selected from stannous 2-ethylhexanoate, zinc 2-ethylhexanoate and mixtures thereof.

Preferably, 0.1 to 10 mole percent of metal compound is used based upon the monomer charge to which the metal compound added. Most preferably, 1 to 3 mole percent of metal compound is used based upon the monomer charge to which the metal compound is added. Such metal compound accelerator can be added to the dental composition mixture prior to the exposure of the dental composition mixture to the radiant energy source.

Photosensitizers

It may sometimes be advantageous to add to the dental composition an effective amount of a photosensitizer in order to obtain efficient transfer of radiation. Such photosensitizer can be added to the dental composition mixture prior to the exposure of the dental composition mixture to the radiant energy source. Examples of such photosensitizers are ketones, α-diketones, α-β-unsaturated ketones coumarins, and the like. Preferably, the photosensitizer utilized comprises camphorquinone for reasons of greater depth of cure. 0.05 to 15 weight percent of a photosensitizer can be added to the dental composition, preferably 0.1 to 5 weight percent.

II. Method of Preparing of Shaped Dental Articles From the Dental Compositions of the Present Invention

The method of preparing the shaped dental articles of the present invention begins with the preparation of the above-described dental compositions useful in forming the shaped dental articles. As indicated above, photoiniferter block polymer selected from the group consisting of I(BT)_n, I(BAT)_n, and mixtures thereof is mixed with free radically polymerizable monomer of the formula C(D)_x, a filler, and other additives such as sensitizers, etc. If needed or desired in order to form the dental composition of the present invention. The dental composition is then partially cured by exposure to a radiant energy source, followed by shaping. The partially cured dental article is then alternately shaped and cured by exposure to the radiant energy source until the desired cure is obtained. A mold may be used to contain and shape the dental composition while it undergoes curing. Depending upon the shaped dental article formed, the mold may preferably be transparent to radiation emitted from the radiant energy source. The radiant energy source utilized should emit ultraviolet or visible radiation in the range of 200 to 800 nm, preferably 300 to 800 nm for extraoral applications for health reasons. If the dental composition is cured in the mouth, visible radiation, from a visible light source such as a Visilux 2™ dental curing light (available from 3M) is preferably used.

As described earlier, the curing of the dental composition to form the shaped dental article is controlled by exposure to a radiant energy source capable of causing the desired extent of polymerization. Suitable radiation sources afford a combination of such properties as safety, controllability, intensity and distribution of incident energy. See generally, "Radiation Curing", Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition, Vol. 19, p. 607-624 (1982). In general, any radiation source capable of emitting radiation of 200 nm to 800 nm can be used. Preferred radiant energy sources are ultraviolet or visible light sources.

Examples

The following detailed description includes exemplary preparations of photoiniferters, photoiniferter block polymers of the formula I(BT)_n, photoiniferter block polymers of the formula I(BAT)_n, and dental compositions produced therefrom which are useful in forming polymeric materials of the type useful as shaped dental articles. All parts and percentages are by weight unless otherwise specified.

Definitions of Terms

The number-average molecular weight (\bar{M}_n), and weight-average molecular weight (\bar{M}_w), are well known mathematical descriptions of the molecular weight distribution of a polymer sample.

The polydispersity, abbreviated "p", is a measure of the molecular weight distribution of a polymer and is defined as \bar{M}_w/\bar{M}_n .

Each of the foregoing is a well known term used by polymer chemists and others. Further explanation of the derivation of these terms may be found in Experimental Methods in Polymer Chemistry, Wiley and Sons, 1981, Chapter 3 entitled "Molecular Weight Averages", pages 57-61.

"Barcol Hardness" is a measurement of hardness. Barcol Hardness measurements were taken of the dental compositions of the present invention at various stages of cure. The Barcol Hardness measurements were taken using a Barcol Hardness Indenter Tester available commercially from the Barber Colman Company, yielding hardness values of the "B" scale. For the following Examples when the Barcol hardness measurement was low (e.g. 0-20) curing was not yet complete and the dental composition material was still carvable. When the Barcol hardness measurement was high (e.g. 30-50) the dental composition material was glassy and nearly fully cured.

EXAMPLES 1-3

Examples 1, 2 and 3 describe the preparation of a monoiniferter compound, a diiniferter compound, and a tetrainiferter compound, respectively, which are useful in preparing photoiniferter block polymers which are useful in the dental composition of the present invention.

EXAMPLE 1

Synthesis of Monofunctional Photoiniferter Benzyl Carbazolydithiocarbamate (CDC)

Into a 250 ml volume flask fitted with a magnetic stirrer and a Dean-Stark trap were charged 35.85 parts of carbazole, 12 parts of potassium hydroxide, and 132 parts of xylene. The mixture was refluxed to remove

water. A light yellow-colored solid, the potassium salt of carbazole, was removed by suction filtration. An excess of carbon disulfide was added to 21.7 parts of potassium carbazole dissolved in 100 parts of dimethyl formamide. A mildly exothermic reaction occurred and the resultant solution was stirred overnight at room temperature. A dark maroon colored solution was obtained. The addition of 13.3 parts of benzyl chloride changed the color of the solution to that of a lighter maroon. After stirring the solution for about 5 hours, the reaction was quenched with water. Next, 100 parts of methylene chloride was added and the reaction mixture was washed three times with water. The organic layer was dried over anhydrous magnesium sulfate and filtered. Upon concentration of the filtrate under vacuum, a bright yellow-colored solid was obtained. The solid was recrystallized from diethyl ether:hexanes. Nuclear magnetic resonance spectroscopy confirmed the presence of pure benzyl carbazolyldithiocarbamate, m.p. 66-68°C.

EXAMPLE 2

15 Synthesis of Difunctional Photoiniferter Xylylene bis(N,N-diethyldithiocarbamate) (XDC)

Into a 1-liter three-necked flask fitted with a mechanical stirrer were charged 89.7 parts of 2,2'-dichloro-p-xylylene and 764 parts of ethanol. Next, 235 parts diethyl dithiocarbamic acid sodium salt (C_2H_5)₂NCS₂Na·3H₂O were charged into the flask. The mixture was stirred at room temperature for about three hours. A heavy solid precipitate of sodium chloride was observed. Next, 444 parts of chloroform were added to the reaction mixture and the solution was stirred overnight. The reaction mixture was then filtered to remove the sodium chloride precipitate. The filtrate was placed in a 1,000 ml volume flask and the solvent removed by rotary evaporation. The solid obtained was dissolved in chloroform and washed four times with water. The chloroform layer was dried over anhydrous magnesium sulfate and filtered following which the solvent was removed by rotary evaporation. The white solid obtained was recrystallized from ethanol. Nuclear magnetic resonance spectroscopy confirmed the presence of pure XDC compound, m.p. 78-80°C.

EXAMPLE 3

30 Synthesis of Tetrafunctional Photoiniferter - durene $\alpha,\alpha',\alpha'',\alpha'''$ -tetrakis-dithiocarbamate (DDC)

Into a 500 ml round-bottom flask was charged 25 parts of durene, 133 parts of N-bromosuccinimide, 175 parts of carbon tetrachloride and 0.83 parts benzoyl peroxide. The mixture was refluxed for about four hours and subsequently filtered. The filtrate was concentrated by rotary evaporation and the residual solid was recrystallized from diethyl ether. Nuclear magnetic resonance spectroscopic analysis of the solid confirmed the presence of $\alpha,\alpha',\alpha'',\alpha'''$ -tetrabromodurene (TBD). To 2.36 parts of TBD and 26 parts of tetrahydrofuran contained in a 100 ml flask were added 4.8 parts of sodium diethyldithiocarbamate dissolved in 17 parts of tetrahydrofuran. Sodium bromide precipitated out immediately as a white solid. After stirring for about four hours at room temperature, the reaction mixture was filtered to remove the sodium bromide precipitate. The filtrate was concentrated by rotary evaporation and the residual waxy solid was recrystallized from ethanol to yield a white crystalline solid. Nuclear magnetic resonance spectroscopic analysis confirmed the structure to be durene $\alpha,\alpha',\alpha'',\alpha'''$ -tetrakis-dithiocarbamate.

EXAMPLES 4-8

45 Examples 4, 5 and 8 describe the preparation of photoiniferter block polymers of the formula I(BT)_n utilizing the difunctional photoiniferter compound of Example 2, the monofunctional photoiniferter compound of Example 1, and the tetrafunctional photoiniferter compound of Example 3, respectively.

60 EXAMPLE 4

Synthesis of Xylene bis(N,N-diethyldithiocarbamate) (XDC)-poly MMA [I(BT)_n] n=2

55 Into a 237 ml clear flint glass bottle were charged 30 parts of methyl methacrylate (MMA), 0.53 parts of xylene bis (N,N-diethyldithiocarbamate) [XDC] prepared according to the procedure of Example 2, and 30 parts of ethyl acetate. The solution was purged with nitrogen gas for about 10 minutes, following which the bottle was sealed, placed on a roller mill, and irradiated with a bank of six General Electric (GE) 15 watt cylindrical black light lamps. The mixture became progressively more viscous. The completion of the reaction was monitored by nuclear magnetic resonance spectroscopy and gas chromatography until the presence of

monomer could no longer be detected. Analysis by gel permeation chromatography (GPC) showed the XDC-poly MMA to have a number average molecular weight of 42,183 and a polydispersity of 1.82.

6 EXAMPLE 5

Synthesis of Carbazole-N-dithiocarbamate (CDC)-poly MMA [I(BT)_n] n=1

Into a 237 ml clear flint glass bottle were charged 25 parts of methyl methacrylate, 1.0 part of monofunctional photoiniferter carbazolyldithiocarbamate (CDC) prepared according to the procedure of Example 1, and 30 parts of ethyl acetate. The solution was purged with nitrogen gas for about 10 minutes after which the bottle was sealed and irradiated as described in Example 4. After completion of the polymerization, the reaction mixture was diluted with a large excess of methanol. A fine light yellow solid precipitate was obtained. The precipitate was isolated by filtration and dried. Molecular weight determination by GPC showed $\bar{M}_n = 27,943$, $\bar{M}_w = 47,161$ and polydispersity of $p = 1.69$ with absorption at 250-450 nm.

EXAMPLE 6

Synthesis of durene $\alpha,\alpha',\alpha'',\alpha'''$ -tetrakis dithiocarbamate (DDC)-poly MMA [I(BT)_n] n=4

Into a 237 ml clear flint glass bottle were charged 10 parts of methyl methacrylate, 0.38 part of the tetrafunctional photoiniferter durene $\alpha,\alpha',\alpha'',\alpha'''$ -tetrakis-dithiocarbamate (DDC) prepared according to the method of Example 3, and 15 parts of ethyl acetate. The solution was purged with nitrogen gas for 10 minutes and irradiated as described in Example 4. The resulting solution was diluted with 200 parts of methanol upon which the polymer precipitated. The polymer was subsequently isolated by filtration and dried in a vacuum oven at 50°C. GPC analysis showed the $\bar{M}_n = 28,000$ and the polydispersity = 2.0.

EXAMPLES 7-9

Examples 7-9 relate to the synthesis of triblock copolymers of the formula I(BAT)_n formed utilizing the difunctional photoiniferter compound of Example 2. The triblock copolymers of Examples 7-9 are useful for inclusion in the dental composition of the present invention.

EXAMPLE 7

Synthesis of copoly(phenethyl methacrylate-butyl acrylate-phenethyl methacrylate) Triblock Copolymer [PEMA - BA - PEMA 10:80:10] [I(BAT)_n] n=2

Into a 355 ml clear glass flint bottle were charged 100 parts of butyl acrylate (BA), 1.5 parts of xylylene-dithiocarbamate (XDC) prepared according to the method of Example 2, and 130 parts of ethyl acetate. The solution was purged with nitrogen gas and irradiated according to the method set forth in Example 4. The reaction mixture became progressively more viscous. The completion of the reaction was monitored by nuclear magnetic resonance spectroscopy until the vinyl peaks could no longer be detected. GPC analysis revealed the polybutyl acrylate-XDC to have a $\bar{M}_n = 42,400$ and a polydispersity = 2.7. Into a 237 ml clear flint glass bottle were charged 46 parts of the above isolated polyBA-XDC, [I(BT)_n], 5 parts of phenethyl methacrylate (PEMA), and 76.5 parts of ethyl acetate. After purging for 10 minutes with nitrogen gas and sealing the bottle, the mixture was irradiated for 40 hours in a roller mill with six General Electric (GE) 15 Watt fluorescent lamps. The polymer was then precipitated by the addition of 400 parts of methanol. The precipitated polymer was separated by filtration and dried in a vacuum oven at 50°C.

EXAMPLE 8

Synthesis of Copoly(isobornyl methacrylate-butyl acrylate-isobornylmethacrylate) Triblock Copolymer [IBoMA - BA - IBoMA 10:80:10] [I(BAT)_n] n=2

Into a 355 ml clear flint glass bottle were charged 46 parts of polybutyl acrylate-XDC, [I(BT)_n], prepared according to the method of Example 7, 5 parts of isobornyl methacrylate, and 76.5 parts of ethyl acetate. The solution was purged and irradiated and the polymer isolated and dried as described in Example 7.

EXAMPLE 9Synthesis of Copoly(methyl methacrylate-butyl acrylate-methyl methacrylate 25:50:25) Triblock Copolymer [I(BAT)_n] n=2

Into a 355 ml clear flint glass bottle were placed 113 parts of butyl acrylate, 1.5 parts of difunctional photoiniferter xylene bis(N,N-diethyldithio carbamate) (XDC), prepared according to the method of Example 2, and 113 parts of toluene. The solution was purged with nitrogen gas for 10 minutes and irradiated according to the procedure set forth in Example 4 for 24 hours. Into a 237 ml clear flint glass bottle were charged 53.1 parts of the polybutyl acrylate-XDC obtained above, 40 parts of methyl methacrylate, and 43.7 parts of toluene. The resultant solution was purged and irradiated according to the procedure set forth in Example 4 for 19 hours. The polymer was precipitated by the addition of 400 parts of methanol, separated by filtration, and dried in a vacuum oven at 50°C. Nuclear magnetic resonance spectroscopic analysis revealed the butyl acrylate to methyl methacrylate mole ratio to be 50:50.

EXAMPLES 10-14

Examples 10-14 relate to dental composition experiments which for simplicity reasons did not include a filler.

COMPARATIVE EXAMPLE 10Involving the Polymerization of TEGDMA in the Presence and Absence of XDC-PMMA

A 5 gram portion of the solution of photoiniferter block polymer XDC-PMMA [I(BT)_n] of Example 4 was precipitated in 25 ml of diethyl ether by rapid stirring. The precipitated white polymer was filtered, washed with diethyl ether, and dried in *vacuo*. The precipitated photoiniferter block polymer XDC-PMMA was then dissolved in 5.7 parts of triethyleneglycol dimethacrylate (TEGDMA) C(D)_x monomer in a glass bottle in order to form a dental composition. No initiators or sensitizers were included in the dental composition. The resultant dental composition was irradiated in a Kulzer curing chamber (available from Kulzer Dental Company) fitted with a pulsed xenon lamp having a minimum wattage of 45 watts and a maximum wattage of 1300 watts. After 90 seconds of irradiation, a gelled material was observed. This gelled material was subjected to a second 90 second exposure, resulting in the formation of a hard set material.

A control experiment was performed which involved the irradiation of TEGDMA alone. 5.7 parts of TEGDMA was placed in a bottle which was irradiated in the Kulzer curing chamber for 90 seconds. No gelation was observed after the first 90 second exposure and following the second 90 second exposure only a trace of gelation was observed. Comparative Example 10 thus demonstrates that photoiniferter block polymer XDC-PMMA can induce the polymerization of C(D)_x monomer upon exposure to ultraviolet radiation.

EXAMPLE 11Curing of XDC-poly MMA in Combination with Various C(D)_x Monomers

The precipitated XDC-Poly MMA [I(BT)_n] prepared according to the method of Example 10 was dissolved in a number of different C(D)_x monomers as shown in Table I below, in order to form viscous dental composition Samples 11a-e.

TABLE I

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<u>Sample</u>	<u>C(D)x</u>	<u>Parts of</u>	<u>Parts of</u>
	<u>Monomer</u>	<u>Monomer</u>	<u>XDC-PMMA</u>
11a	TEGDMA	1	1.77
11b	Butyl acrylate	1	2.5
11c	Butyl acrylate	4	1.0
11d	Phenethyl methacrylate	1	2.5
11e	Norbornyl acrylate	4	1.0

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Each of the above Samples 11a-e were transferred to the pulsed xenon lamp curing unit described in Example 10. 3.888 grams of each sample was placed in a separate open glass vial. The xenon lamp curing unit was flushed with nitrogen gas for one minute and then subjected to a nitrogen pressure of 1.16×10^{-2} Pascals. Sequential 90 second exposures were used to irradiate each sample. A filter was used to eliminate radiation below 280 nm and above 850 nm. The nature of each irradiated sample after each exposure was rated in terms of consistency. The ratings for Samples 11a-e are provided in the Remarks Section of Table II below.

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TABLE II

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<u>Sample</u>	<u>Number of 90 Second Exposures</u>	<u>Remarks</u>
11a	1	Soft putty
	2	Hard putty, carvable
	3	Hard, glassy, Barcol 46/46
11b	1	Hard material
11c	1	Butylacrylate lost by evaporation
11d	1	Viscosity increased
	2	Soft putty
	3	Hard putty
	4	Carvable
11e	5	Hard, glassy, Barcol 35/30
	1	Heavy consistency
	2	
	3	Soft putty
	4	Carvable
	5	Hard, but still carvable
	6	Glassy

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Example 11 demonstrates that the physical nature of the dental composition can be controlled by controlling the exposure of the dental composition to the radiation source. Thus, after 2 exposures the dental composition Sample 11d cured to a soft putty, after 3 exposures it obtained a consistency such that it was harder and shapeable, after 4 exposures it was carvable, and after 5 exposures its shape was fixed.

The purpose of Examples 12, 13 and 14 was to demonstrate whether the radiant energy source curing of

a dental composition could take place in the absence of a photoiniferter block polymer.

EXAMPLES 12 AND 13 AND COMPARATIVE EXAMPLE 14

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The solutions used for Examples 12-14 are set forth in Table III below. Approximately 0.4 ml portions of each of the solutions were placed in separate 0.38 cm Teflon™ molds, each mold having a 7 mm diameter and a 2.5 mm deep cylindrical hole through the center thereof. Polyester sheets each having a thickness of 0.05 mm were placed on the top and bottom surfaces of the mold to exclude air and squeeze out excess solution.

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The solutions contained in each mold were then separately irradiated for specified time periods with a Visilux™ 2 dental curing light (available from 3M). A Barcol hardness evaluation of the top (exposed) and bottom surfaces of the samples was performed using an indenter available commercially from the Barber Colman Company, yielding hardness values of the "B" scale.

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TABLE III

Example	Solution Composition (parts)	Irradiation Time (sec.)	Properties	Barcol Hardness Top/Bottom
12	CDC-poly MMA	1	Firm, carvable	*
	TEGDMA	1.5	Harder	10/8
	BIS-GMA	1.5	Glassy	35/32
	Camphorquinone	0.02		
13	DDC-poly MMA	1	Hard	20/8
	TEGDMA	1.5	Glassy	40/38
	BIS-GMA	1.5		
	Camphorquinone	0.02		
14	TEGDMA	1.5	No cure	*
	BIS-GMA	1.5		
	Camphorquinone	0.02		

* No reading with the Barcol hardness tester was obtainable.

The data contained in Table III demonstrates that a photoiniferter system is essential for the curing reaction to occur since the composition of Example 14 which did not contain a photoiniferter did not cure.

EXAMPLE 15**Preparation and Curing of a Dental Composition Useful as a Restorative**

The following ingredients were charged into a glass vial:

Copoly(IBOMA-BA-IBOMA) (of Example 8)	6.48	parts
Isobornyl methacrylate	6.48	parts
Triethyleneglycol dimethacrylate	3.00	parts
BIS-GMA	3.00	parts
Camphorquinone	0.092	parts

The glass vial was then sealed and placed on a roll mill for about 4 hours in order to form a homogeneous solution. To 14.82 parts of the resulting homogeneous solution were added 4.81 parts of diatomaceous silica and 1.40 parts of precipitated silica in order to form a mixture. The mixture was spatulated in order to provide a smooth paste. A portion of the paste was placed in a 3.8 cm x 0.762 cm x 0.127 cm rectangular plexiglass mold which was then placed in a specially designed curing unit. The specially designed curing unit was equipped with a high intensity 650 watt tungsten halogen light source which emitted radiation. In addition, the curing unit was equipped with optional pressure and vacuum curing cycles. The curing unit utilized an external vacuum pump and in addition was attached to a pressurized air source of $2.75 - 4.0 \times 10^6$ Pascals. The light source exposure settings were capable of being varied. The actual time of illumination of the curing unit chamber corresponding to the switch settings (1 - 10) are set forth below.

Time of Illumination of Curing Unit Chamber

<u>Switch Setting</u>	<u>Time (Min:secs.)</u>
1	0:25
2	0:32
3	0:42
4	0:55
5	1:11
6	1:33
7	2:01
8	2:37
9	3:24
10	4:25

The sample composition was subjected to exposures of "light only" in the curing unit chamber at setting 3 (42 second exposure). The properties of the sample composition were measured initially by indentation with a 300 gram Gilmore needle and are described in Table IV. The sample was allowed to stand at ambient conditions for 1 minute between exposures.

TABLE IV

Number of Exposures	Total Exposure Time(min:sec.)	Properties
1	0:42	Soft, flowable
2	1:24	Putty-like
3	2:06	Firm, indentable
4	2:48	Firm, elastic
5	3:30	Hard, not indentable

After 3 exposures the sample composition could be shaped at which point it was at a consistency which would be useful in forming a denture base or a restorative. After 4 exposures it could be carved at which point it would be useful for final fitting as a denture base. After exposure 5, the final shape was fixed. The data contained in Table IV demonstrates controlled curing of a restorative dental composition.

EXAMPLE 16

Preparation of a Dental Composition Useful as a Denture Liner

Into a glass vial were charged the following:

Copoly(phenethyl methacrylate- butyl acrylate-phenethyl methacrylate) (10:80:10) (of Example 7)	7.74 parts
Isobornyl methacrylate	7.74 parts
BIS-GMA	3.00 parts
Triethyleneglycol dimethacrylate	3.00 parts
Camphorquinone	0.108 part

The contents of the glass bottle were mixed by sealing the glass bottle and roll milling the bottle for about 4 hours in order to yield a homogenous solution.

To 14.82 parts of the resulting homogeneous solution were added 4.79 parts of diatomaceous silica and 1.41 parts of precipitated silica. The mixture was spatulated to provide a smooth paste. A portion of the paste was cured as described in Example 15. The results are set forth in Table V.

TABLE V

Number of Exposures	Total Exposure Time (min.:sec.)	Properties
1	0:42	Soft
2	1:24	Putty-like, carvable
3	2:06	Firm, slight indentation
4	2:48	Firm, no indentation
5	3:30	Firm, no indentation

The tensile strength, percent elongation and modulus of the sample prepared according to Example 16 are reported in Table VII below.

EXAMPLE 17**Preparation of a Dental Composition Useful as a Denture Base**

Into a glass vial were charged the following:

10	Copoly(methyl methacrylate-butyl acrylate-methyl methacrylate) [25:50:25] (of Example 9)	8.0 parts
	Isobornyl methacrylate	5.0 parts
	BIS-GMA	3.5 parts
15	Triethyleneglycol dimethacrylate	3.5 parts
	Camphorquinone	0.1 parts

The glass vial was then sealed and placed on a roll mill for about 6 hours in order to form a homogeneous solution. To the resulting homogeneous solution was added 1.3 parts of Cab-O-Sil fumed silica (available from Cabot Corporation) in order to form a mixture. The mixture was spatulated in order to provide a smooth paste. A portion of the dental composition paste was cured as described in Example 15.

Table VI below sets forth the properties of the dental composition paste of Example 17 after exposure in the curing unit chamber.

TABLE VI

30	Number of Exposures	Total Exposure Time (min.:sec.)	Properties
	1	0:42	Soft
	2	1:24	Firm, putty-like, carvable
	3	2:06	Hard
35	4	2:48	Hard, glassy

The data contained in Table VI demonstrates the effect of controlled curing on the properties of the dental composition. The tensile strength, percent elongation and modulus of the dental composition sample prepared according to Example 17 are reported in Table VII below.

Measurement of Tensile Properties

The tensile properties of the dental compositions prepared according to Examples 15-17 were measured after the fourth and fifth successive exposures. The sample preparation was as follows. Portions of the dental composition pastes prepared according to Examples 15-17 were packed into three separate rectangular plexiglass molds, each mold having a length of 3.81 centimeters, a width of 0.762 centimeter, and a thickness of 0.127 centimeter. The top of each mold was then covered with a plexiglass plate and a 300 gram weight was placed on each plexiglass plate in order to remove air bubbles from the paste samples. The weights were then removed and each paste sample was separately placed in the curing unit and exposed at the desired cycle for the appropriate time periods. After the exposures were completed the samples were allowed to stand for approximately 1 hour at 37°C. and 95% relative humidity, and subsequently removed from the molds. In some instances a silicone die-release material was used on the inside of the molds in order to facilitate removal of the cured paste sample. Two marks were placed on each cured paste sample at a distance of 2.54 centimeters apart. The cured paste samples were then placed in distilled water and aged at 37°C. for 24 hours. The cure paste samples were then clamped in an Instron™ testing machine so that the jaws of the Instron testing machine were aligned along the two marks. This ensured that the distance of separation of the jaws was always 2.54 cm. The properties of the cured paste samples were then tested in tension. The following formulae were used for calculating the numerical values of the properties measured.

$$\text{Tensile} = \frac{\text{Force at Break}}{\text{Width} \times \text{Thickness}}$$

$$\text{Modulus} = \frac{\text{Force} \times \text{Initial Length}}{\text{Width} \times \text{Thickness} \times \text{Final Length}}$$

$$\% \text{ Elongation at break} = \frac{\text{Final Length} - \text{Original Length}}{\text{Original Length}} \times 100$$

The elongation, tensile strength and modulus of the paste samples prepared according to Examples 15-17 which had been cured after four and five exposures at setting 3 are set forth in Table VII. Measurements could not be taken after exposures one, two, and three since sufficient polymerization and crosslinking had not yet occurred.

An examination of the values obtained reveals that further curing occurred with additional exposure as evidenced by the increase in tensile strength and modulus and the decrease in elongation as the exposure continued. The paste samples after the fourth and fifth exposures exhibited properties which would make them suitable for use as denture liners.

TABLE VII

Tensile Properties of the Cured Dental Composition

Samples of Examples 15-17

Ex.	Number of Exposures	Total Exposure Time (min:sec)	Elongation (%)	Tensile Strength (MPa)	Modulus (MPa)
15	4	2:48	72	2.075	0.421
15	5	3:30	59	3.192	0.656
16	4	2:48	65	2.213	0.408
16	5	3:30	48	3.364	0.586
17	3	2:06	27	10.775	641.142
17	4	2:48	6	43.439	1371.906

EXAMPLE 18

Preparation of a Dental Composition Useful as a Dental Restorative

Into a glass bottle were charged the following:

Copoly(methyl methacrylate-butyl acrylate-methyl methacrylate) (25:50:25) (from Example 9)	37.5 parts
Methyl methacrylate	22.5 parts
BIS-GMA	19.8 parts
Triethyleneglycol dimethacrylate	19.8 parts
Camphorquinone	0.3 parts

The glass bottle was then sealed and placed in a mechanical shaker for about 18 hours in order to provide a homogeneous solution. To 67 parts of the homogeneous solution were added 113 parts of a mixture of zirconia:silica filler (5.5:1 mole ratio of $\text{SiO}_2:\text{ZrO}_2$ filler prepared for filtered sols according to the method described in U.S. Pat. No. 4,503,169, incorporated by reference herein, and containing 20% "OX-50"™ submicron filler) which had previously been treated with gamma-methacryoxy-propyltrimethoxy silane. A smooth dental composition paste was prepared by spatulation. A portion of the dental composition paste was placed in two separate 0.38 cm³ Teflon™ polytetrafluoroethylene molds, each mold having a 7 mm diameter and a 2.5 mm deep

cylindrical hole through the center thereof. Polyester sheets (2 mil thick) were placed on the top and bottom of each mold to exclude air and squeeze out excess paste. The paste samples were then irradiated with a Visilux™ 2 dental curing light for various periods of time. The two paste samples were sequentially cured. After 5 seconds of exposure, each paste sample was of the consistency of a soft, packable putty. After 10 additional seconds (15 seconds total) each paste sample was carvable, but still indentable by a 300 gram Gilmore needle. After an additional 10 seconds of exposure (25 seconds total), hard cured paste samples were obtained. Measurement of the Barcol hardness for both cured paste samples yielded a mean average value of 75 for the top sides for both paste samples and a mean average value of 68 for the bottom sides of both samples.

For diametral tensile strength measurements, uncured paste was packed into five separate glass tubes, each tube having a 4 mm inner diameter. Each paste sample was then subjected to 2.75×10^5 Pascals pressure for 5 minutes and cured by exposure to a Visilux™ 2 curing light. The cured pastes from each sample were cut on a diamond saw to form 2 mm long cylindrical plugs. The plugs were stored in distilled water at 37°C. for 24 hours after which their diametral tensile strengths were determined according to ADA (American Dental Association) specification No. 27 using an Instron tensile tester. The compressive strength was determined for five samples similarly prepared, although each sample was cut to a length of 8 mm according to ADA specification No. 9. The diametral tensile and compressive strength mean average values for the cured paste samples are provided in Table VIII.

EXAMPLE 19

Preparation of a Dental Composition Useful as a Dental Restorative

Into a clear glass flint bottle were charged the following:

XDC-PMMA (prepared according to Example 4)	37.1 parts
Norbornyl acrylate	41.9 parts
Triethyleneglycol dimethacrylate	21.0 parts
Camphorquinone	0.5 parts

The contents of the glass bottle were mixed by sealing the bottle and roll milling the sealed bottle to yield a homogeneous solution. Two parts of the homogeneous solution and 13.3 parts of the filler mixture used in Example 18 were combined and spatulated in order to provide a smooth paste. Curing of a portion of the paste in a 0.38 cm³ Teflon™ polytetrafluoroethylene mold having a circular hole 2.5 mm deep and a 7 mm diameter using a Visilux™ 2 dental curing light available from 3M Company yielded a hard mass in 10 seconds. Results of the curing of the paste sample are reported in Table VIII, Example 19.

Another portion of the paste was then cured in an identical mold at Setting 1 in the curing unit described in Example 15. Results of curing of the paste sample of Example 19 in the curing unit of Example 15 are reported in Table IX.

TABLE VIII

Example	Compressive Strength (MPa)	Diametral Tensile Strength (MPa)	Barcol Hardness
			Top/Bottom
18	403	71.7	75/68
19	422	83.4	85/85

TABLE IX

<u>Number of Exposures</u>	<u>Total Exposure Time (Minutes:seconds.)</u>	<u>Properties</u>	<u>Barcol Hardness Top/Bottom</u>
1	0:25	Soft, carvable	
2	0:50	Firm, carvable	
3	1:15	Hard	70/65
4	2:40	Hard	85/85

The physical property measurements of the dental composition after final cure are described in Table VIII.

EXAMPLE 20Preparation of a Dental Composition Useful as a Dental Restorative

Into a clear glass flint bottle were charged the following:

DDC-MMA (prepared according to Example 6)	37.0 parts
Norbornyl methacrylate	42.0 parts
TEGDMA	21.0 parts
Champhorquinone	0.5 parts

The contents of the glass bottle were mixed by sealing the glass bottle and roll milling the bottle in order to yield a homogeneous solution. To 2 parts of the resulting solution were added 13.3 parts of the filler mixture of Example 18 after which the resultant mixture was spatulated in order to provide a smooth paste. A portion of the paste was placed in a 0.38 cm³ volume Teflon™ mold having a 7 mm diameter and a 2.5 mm deep cylindrical hole through the center thereof. The paste was then cured in the curing unit as described in Example 15. The Barcol Hardness results are provided in Table X below.

TABLE X

<u>Number of Exposures</u>	<u>Total Exposure Time (Minutes:seconds)</u>	<u>Properties</u>	<u>Barcol Hardness Top/Bottom</u>
1	0:25	Firm putty	
2	0:50	Hard	45/42
3	1:15	Hard	85/85

EXAMPLES 21-22

Examples 21 and 22 relate to experiments involving the effect of a metal compound accelerator on the polymerization of dental compositions which did not contain a filler for simplicity reasons.

EXAMPLE 21Control Experiment Involving the Preparation of a Dental Composition in the Absence of Sn(Oct)₂ Metal Compound Accelerator

Into a 237 ml glass bottle were charged the following:

Block copoly(methyl methacrylate- methacrylate) [25:50:25] (from Example 9)	37.5 parts
Methyl methacrylate	22.5 parts
BIS-GMA	19.8 parts
Triethyleneglycol dimethacrylate	19.8 parts

The contents of the glass bottle were mixed by sealing the glass bottle and roll milling the bottle for several hours in order to yield a homogeneous solution. Next, 13.8 parts of the homogeneous solution was placed in a circular pan having a diameter of 6.6 mm and a depth of 1.6 mm which was then placed in the photocell chamber of a Differential Photocalorimeter (Model # 930, E. I. du Pont De Nemours & Co.). The cell was maintained under a nitrogen atmosphere and the sample was irradiated with a 200 Watt mercury lamp for 2 minutes. The enthalpy was measured since enthalpy is directly proportional to the rate of polymerization. The observed enthalpy was 29.1 J/g.

EXAMPLE 22

Preparation of a Dental Composition in the Presence of $\text{Sn}(\text{Oct})_2$ Metal Component Accelerator
Into a 237 ml glass bottle were charged the following:

Block copoly(methyl methacrylate- butyl acrylate-methyl methacrylate) [25:50:25] (from Example 9)	37.5 parts
Methyl methacrylate	22.5 parts
BIS-GMA	19.8 parts
Triethyleneglycol dimethacrylate	19.8 parts
Stannous 2-ethyl hexanoate (Accelerator Compound)	12.3 parts

The contents of the glass bottle were mixed by sealing the glass bottle and roll milling the bottle for several hours in order to yield a homogeneous solution. Next, 14.5 parts of the homogeneous solution were placed in a circular pan having a diameter of 6.6 mm and a depth of 1.6 mm. The pan containing the solution was then placed in the photocell chamber of a Differential Photocalorimeter as described in Example 21. The cell was maintained under a nitrogen atmosphere and the sample was irradiated with a high pressure mercury lamp for 2 minutes. The observed enthalpy was 79.7 J/g indicating a higher reaction rate when a metal compound accelerator compound is used. The use of a metal compound accelerator resulted in a 2.7 times faster reaction rate.

Claims

1. A dental composition comprising:
a mixture of

(i) acrylic photoiniferter block polymer selected from $\text{I}(\text{BT})_n$, $\text{I}(\text{BAT})_n$, and mixtures thereof, wherein
I represents the free radical initiator portion of an iniferter of the formula $\text{I}(\text{T})_n$;
T represents the terminator portion of said iniferter;
n is an integer of 1 to 12.

B represents an acrylic polymer block having a glass transition temperature ranging from -200°C to 400°C ; and

A represents a normally thermoplastic polymer block having a glass transition temperature of at least 30°C ;

(ii) a monomer charge comprising free radically polymerizable monomer of the formula $\text{C}(\text{D})_x$ wherein
x is an integer ranging from 1 to 9;

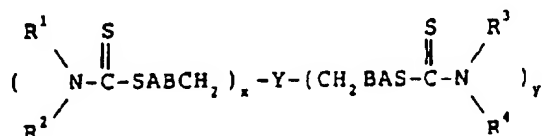
D is an ethylenically unsaturated monovalent moiety; and

C is an organic residue; and

(iii) 5 to 90 weight % of a filler based upon the weight of said mixture;

wherein the weight ratio of photoiniferter block polymer to free radically polymerizable monomer of the formula $C(D)_x$ ranges from 1:99 to 99:1, and wherein controlled and intermittent exposure of said mixture to a radiant energy source capable of emitting radiation in a range of 200 to 800 nm results in the partial polymerization or crosslinking of the acrylic photoiniferter block polymer and free radically polymerizable monomer of the formula $C(D)_x$ in order to form a partially cured dental article capable of being shaped, after which a final exposure to said radiant energy source provides a final cured dental article.

2. The dental composition of Claim 1 wherein said photoiniferter block polymer has the formula $I(BAT)_n$ and wherein polymer block B has a glass transition temperature ranging from -200°C to 100°C , polymer block A has a glass transition temperature ranging from 30°C to 150°C , and the glass transition temperature of polymer block A is about 50°C higher than the glass transition temperature of polymer block B.
3. The dental composition of Claim 1 wherein said acrylic photoiniferter block polymer has the formula $I(BT)_n$.
4. The dental composition of any one of claims 1 and 2 wherein said acrylic photoiniferter block polymer has the formula $I(BAT)_n$ and wherein n is an integer ranging from 2 to 12.
5. The dental composition of any one of claims 1, 2 and 4 wherein said polymer block A is formed from monomer selected from methyl methacrylate, phenethyl methacrylate, isobornyl methacrylate, isopropyl methacrylate, n -propyl methacrylate, and mixtures thereof.
6. The dental composition of any one of claims 1-2 and 4-5 wherein said acrylic photoiniferter block polymer has the formula $I(BAT)_n$ and wherein $I(BAT)_n$ is represented by the formula



wherein

R^1 , R^2 , R^3 and R^4 are aliphatic or aromatic moieties which can be the same or different and which do not substantially interfere with the ability of I- to promote free radical polymerization or with the ability of T- to recombine with I- or a polymer free radical segment including I-;

Y is a linking group having a functionality of $x+y$ which does not substantially interfere with the ability of I- to promote free radical polymerization or the ability of T- to recombine with I- or a polymer free radical segment including I-; and

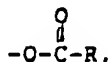
x and y are each integers of at least 1 and the sum of $x+y$ is not greater than 12.

7. The dental composition of any preceding claim wherein said iniferter is selected from benzyl carbazolyldithiocarbamate, xylene bis(N,N-diethyldithiocarbamate), durane $\alpha,\alpha',\alpha'',\alpha'''$ -tetrakis(N,N-diethyldithiocarbamate), xylene carbazolyldithiocarbamate, and mixtures thereof.
8. The dental composition of any preceding claim wherein said free radically polymerizable monomer of the formula $C(D)_x$ is selected from butyl acrylate, phenethyl methacrylate, norbornyl acrylate, isobornyl methacrylate, diglycidyl methacrylate, ethoxylated bisphenol A dimethacrylate, diethylene glycol diacrylate, diethylene glycol methacrylate, triethylene glycol diacrylate, triethylene glycol dimethacrylate, 2,2-dimethylpropane diol diacrylate, 2,2-dimethylpropane diol dimethacrylate, tetraethylene glycol diacrylate, tetraethylene glycol dimethacrylate, hexane diol diacrylate, hexane diol dimethacrylate, ethoxylated bisphenol A diacrylate, ethoxylated bisphenol A dimethacrylate, pentaerythritol trimethacrylate, pentaerythritol tetramethacrylate, and mixtures thereof.
9. The dental composition of any preceding claim which further comprises a polymerization accelerating amount of a metal compound, wherein the metal compound is represented by the general formula M_nL_m wherein

M is a cation having a valency of z of a metal which is selected from tin, zinc, cobalt, titanium, palladium, and lead;

x is an integer of at least 1;

L is an anion having a valency of x which is selected from C₁₋₂₀ alkyl, aryl, -OR,



NO₃, SO₄=, and PO₄³⁻;

R is selected from C₁₋₂₀ alkyl and aryl; and

z is an integer of at least 1.

10. A method of making a dental article comprising the steps of:

(i) forming a mixture of

(a) acrylic photoiniferter block polymer selected from I(BAT)_n, I(BAT)_n, and mixtures thereof, wherein

I represents the free radical initiator portion of an iniferter of the formula I(T)_n;

T represents the terminator portion of said iniferter;

n is an integer of 1 to 12

B represents an acrylic polymer block of suitable molecular weight; and

A represents a normally thermoplastic polymer block having a glass transition temperature of at least 30°C;

(b) a monomer charge comprising free radically polymerizable monomer of the formula C(D)_x, wherein

x is an integer ranging from 1 to 9,

D is an ethylenically unsaturated group, and

C is an organic residue, and

(c) 5 to 90 weight % of a filler based upon the weight of said mixture,

wherein the weight ratio of the acrylic photoiniferter block polymer to free radically polymerizable monomer of the formula C(D)_x ranges from 1:99 to 99:1;

(ii) exposing the mixture to radiation of 200 to 800 nm from a radiant energy source until polymerization or crosslinking of the acrylic photoiniferter block polymer and free radically polymerizable monomer occurs in order to form a partially cured dental article;

(iii) shaping the partially cured dental article of step (ii) as desired;

(iv) repeating steps (ii) and (iii), if necessary, until the desired shape of the partially cured dental article has been obtained; and

(v) exposing the partially cured dental article of either step (iii) or step (iv) to a final exposure of radiation in order to form a final cured dental article.

Patentansprüche

1. Zahnärztliche Zusammensetzung, umfassend eine Mischung von:

(i) acrylischem Photoiniferter-Blockpolymer, ausgewählt aus I(BT)_n, I(BAT)_n und deren Mischungen, worin sind:

I der radikalische Initiatoranteil eines Iniferters der Formel I(T)_n;

T der Terminatorteil des Iniferters;

n eine ganze Zahl von 1 bis 12;

B ein acrylischer Polymerblock mit einer Glasübergangstemperatur im Bereich von -200 °C bis 400 °C und

A ein normalerweise thermoplastischer Polymerblock mit einer Glasübergangstemperatur im Bereich von mindestens 30 °C;

(ii) einer Monomercharge, die ein radikalisch polymerisierbares Monomer der Formel C(D)_x aufweist, worin

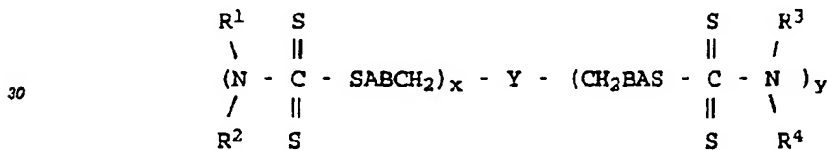
x eine ganze Zahl im Bereich von 1 bis 9 ist;

D eine ethylenisch ungesättigte, einwertige Gruppe ist und

C ein organischer Rest ist; und

(iii) 5 % bis 90 Gewichtsprozent einer Füllmasse bezogen auf das Gewicht der genannten Mischung;

- bei welcher das Gewichtsverhältnis von Photoiniferter-Blockpolymer und radikalisch polymerisierbarem Monomer der Formel $C(D)_x$ im Bereich von 1 : 99 bis 99 : 1 liegt und bei welcher kontrolliertes und intermittierendes Exponieren an einer im Bereich von 200 bis 800 nm emittierenden Strahlung zur partiellen Polymerisation oder Vernetzung des acrylischen Photoiniferter-Blockpolymers und radikalisch polymerisierbaren Monomers der Formel $C(D)_x$ führt, um einen teilweise gehärteten zahnärztlichen Gegenstand zu bilden, der geformt werden kann, wonach ein abschließendes Exponieren an der Strahlungsquelle einen fertigen, gehärteten zahnärztlichen Gegenstand schafft.
2. Zahnärztliche Zusammensetzung nach Anspruch 1, bei welcher das Photoiniferter-Blockpolymer die Formel $I(BAT)_n$ hat und bei welcher Blockpolymer B eine Glasübergangstemperatur im Bereich von -200 °C und 150 °C hat und die Glasübergangstemperatur von Polymerblock A etwa 50 °C höher ist als die Glasübergangstemperatur von Polymerblock B.
 3. Zahnärztliche Zusammensetzung nach Anspruch 1, bei welcher das acrylische Photoiniferter-Blockpolymer die Formel $I(BT)_n$ hat.
 4. Zahnärztliche Zusammensetzung nach Anspruch 1 und 2, bei welcher das acrylische Photoiniferter-Blockpolymer die Formel $I(BAT)_n$ hat und n eine ganze Zahl im Bereich von 2 bis 12 ist.
 5. Zahnärztliche Zusammensetzung nach Anspruch 1, 2 und 4, bei welcher Blockpolymer A aus Monomer gebildet wird, welches ausgewählt wird aus: Methylmethacrylat, Phenethylmethacrylat, Isobornylmethacrylat, Isopropylmethacrylat, n-Propylmethacrylat und deren Mischungen.
 6. Zahnärztliche Zusammensetzung nach Anspruch 1, 2 und 4 und 5, bei welcher das acrylische Photoiniferter-Blockpolymer die Formel $I(BAT)_n$ hat und $I(BAT)_n$ dargestellt wird durch die Formel:



worin sind:

- R^1, R^2, R^3 und R^4 aliphatische oder aromatische Gruppen, welche gleich oder verschieden sein können und die Fähigkeit von I- zur Aktivierung der Radikalpolymerisation oder die Fähigkeit von T- zur Rekombination mit I- oder einem Radikalsegment, einschließlich I-, nicht wesentlich beeinträchtigen;
 - Y eine verbindende Gruppe, welche eine Funktionalität von x+y hat und die Fähigkeit von I- zur Aktivierung der Radikalpolymerisation oder die Fähigkeit von T- zur Rekombination mit I- oder einem Radikalsegment, einschließlich I-, nicht wesentlich beeinträchtigt; und
 - x und y jeweils ganze Zahlen von mindestens 1 und die Summe von x+y nicht größer als 12.
7. Zahnärztliche Zusammensetzung nach einem der vorgenannten Ansprüche, bei welcher der Iniferter ausgewählt wird aus: Benzylcarbazyldithiocarbamat, Xylylenbis(N,N-diethyldithiocarbamat), 1,2,4,5-Tetramethylbenzol- $\alpha, \alpha', \alpha''$ -tetrakis(N,N-diethyldithiocarbamat), Xylylencarbazyldithiocarbamat und deren Mischungen.
 8. Zahnärztliche Zusammensetzung nach einem der vorgenannten Ansprüche, bei welcher das radikalisch polymerisierbare Monomer der Formel $C(D)_x$ ausgewählt wird aus: Butylacrylat, Phenethylmethacrylat, Norbornylacrylat, Isobornylmethacrylat, Diglycidylmethacrylat, ethoxylertes Bisphenol A-dimethacrylat, Diethylenglycoldiacrylat, Diethylenglycoldimethacrylat, Triethylenglycoldiacrylat, Triethylenglycoldimethacrylat, 2,2-Dimethylpropanoldiacrylat, 2,2-Dimethylpropanoldimethacrylat, Tetraethylenglycoldiacrylat, Tetraethylenglycoldimethacrylat, Hexandiolacrylat, Hexandiolmethacrylat, ethoxylertes Bisphenol A-diacrylat, ethoxylertes Bisphenol A-dimethacrylat, Pentaerythritoltrimethacrylat, Pentaerythritoltetra-
 - methacrylat und deren Mischungen.
 9. Zahnärztliche Zusammensetzung nach einem der vorgenannten Ansprüche, ferner umfassend eine polymerisationsbeschleunigende Menge einer durch die allgemeine Formel M_xL_z dargestellten Metallverbin-

dung, worin:

M ein Kation einer Wertigkeit z eines Metalls ist, das ausgewählt wird aus Zinn, Zink, Kobalt, Titan, Palladium und Blei;

x eine ganze Zahl von mindestens 1 ist;

L ein Anion einer Wertigkeit x ist, das ausgewählt wird aus C_{1-20} -Alkyl-, -Aryl-, -OR-, -O-C(O)-R, NO_3 , SO_4^{2-} und PO_4^{3-} ;

R ausgewählt wird aus C_{1-20} -Alkyl-, -Aryl-; und

z eine ganze Zahl von mindestens 1.

10. Verfahren zur Herstellung einer zahnärztlichen Zusammensetzung, umfassend die Schritte:

(i) Schaffen einer Mischung von

(a) acrylischem Photoiniferter-Blockpolymer, ausgewählt aus $I(BT)_n$, $I(BAT)_n$ und deren Mischungen, worin sind:

I der radikalische Initiatoranteil eines Iniferters der Formel $I(T)_n$;

T der Terminatoranteil des Iniferters;

n eine ganze Zahl von 1 bis 12;

B ein acrylischer Polymerblock mit geeignetem Molekulargewicht; und

A ein normalerweise thermoplastischer Polymerblock mit einer Glasübergangstemperatur im Bereich von mindestens 30 °C;

(b) einer Monomercarge, die ein radikalisch polymerisierbares Monomer der Formel $C(D)_x$ aufweist, worin

x eine ganze Zahl im Bereich von 1 bis 9 ist;

D eine ethylenisch ungesättigte Gruppe und

C ein organischer Rest ist; und

(c) 5 % bis 90 Gewichtsprozent einer Füllmasse bezogen auf das Gewicht der genannten Mischung, bei welcher das Gewichtsverhältnis von Photoiniferter-Blockpolymer und radikalisch polymerisierbarem Monomer der Formel $C(D)_x$ im Bereich von 1 : 99 bis 99 : 1 liegt;

(ii) Exponieren der Mischung an einer Strahlungsquelle mit einer Strahlung von 200 nm bis 800 nm bis zum Auftreten einer Polymerisation oder Vernetzung des acrylischen Photoiniferter-Blockpolymers und radikalisch polymerisierbaren Monomers, um einen teilweise gehärteten zahnärztlichen Gegenstand zu bilden;

(iii) Formen des teilweise gehärteten zahnärztlichen Gegenstands von Schritt (ii) nach Bedarf;

(iv) Wiederholen der Schritte (ii) und (iii), sofern erforderlich, bis die gewünschte Form des zahnärztlichen Gegenstands erhalten wird; und

(v) Exponieren des teilweise gehärteten zahnärztlichen Gegenstands von Schritt (iii) oder Schritt (iv) an einer abschließenden Bestrahlung, um einen fertigen, gehärteten zahnärztlichen Gegenstand zu schaffen.

Revendications

1. Composition dentaire comprenant un mélange de :

(i) un polymère bloc acrylique photoiniferté choisi parmi $I(BT)_n$, $I(BAT)_n$, et leurs mélanges où

I représente une portion initiatrice de radicaux libres d'un matériau iniferté ;

T représente la portion terminale dudit matériau iniferté

n est un nombre entier ayant pour valeur 1 à 12 ;

B représente un bloc polymère acrylique ayant une température de transition vitreuse se situant dans le domaine de -200°C à +400°C; et

A représente un bloc polymère normalement thermoplastique ayant une température de transition vitreuse d'au moins +30°C ;

(ii) une charge monomère comprenant un monomère radicalairement polymérisable de formule $C(D)_x$, dans laquelle

x est un nombre entier ayant pour valeur 1 à 9 ;

D est un reste monovalent éthyléniquement insaturé ; et

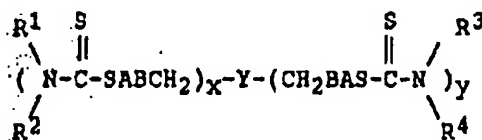
C est un reste organique ; et

(iii) de 5 à 80 % en poids d'une charge, par rapport au poids total dudit mélange ;

où le rapport pondéral du polymère bloc acrylique photoiniferté au monomère radicalairement polymérisable de formule $C(D)_x$ se situe dans l'intervalle de 1/99 à 99/1, l'exposition contrôlée et intermittente dudit

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x et y sont chacun des nombres entiers valant au moins 1 et tels que la somme $x+y$ ne soit pas supérieure à 12.

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9. Composition dentaire suivant l'une quelconque des revendications précédentes, comprenant en outre une quantité d'un composé métallique accélérant la polymérisation, ledit composé métallique répondant à la formule générale $M_x L_z$ où
- 5 M est un cation de valence z d'un métal qui est choisi parmi l'étain, le zinc, le cobalt, le titane, le palladium et le plomb ;
 x est un nombre entier ayant une valeur d'au moins 1 ;
 L est un anion de valence x qui est choisi parmi les alkyle en C_{1-20} , aryle, -OR, -O-C(=O)-R, NO_3^- , SO_4^{2-} et PO_4^{3-} ;
- 10 R est choisi parmi les alkyle en C_{1-20} et aryle ; et
 z est un nombre entier ayant une valeur d'au moins 1.
10. Procédé pour préparer un article dentaire, ledit procédé comprenant les étapes de
- (i) la formation d'un mélange de
- 15 (a) un polymère bloc acrylique photoinféré choisi parmi I(BT)_n, I(BAT)_n et leurs mélanges où
 I représente une portion initiatrice de radicaux libres d'un matériau inféré ;
 T représente la portion terminale dudit matériau inféré
 n est un nombre entier ayant pour valeur 1 à 12 ;
 B représente un bloc polymère acrylique ayant une température de transition vitreuse se situant dans le domaine de -200°C à +400°C ; et
- 20 A représente un bloc polymère normalement thermoplastique ayant une température de transition vitreuse d'au moins +30°C ;
 (b) une charge monomère comprenant un monomère radicalairement polymérisable de formule C(D)_x dans laquelle
- 25 x est un nombre entier ayant pour valeur 1 à 9 ;
 D est un reste monovalent éthyléniquement insaturé ; et
 C est un reste organique ; et
- (c) de 5 à 80 % en poids d'une charge, par rapport au poids total dudit mélange ;
 où le rapport pondéral du polymère bloc acrylique photoinféré au monomère radicalairement polymérisable de formule C(D)_x se situe dans l'intervalle de 1/99 à 99/1 ;
- 30 (ii) l'exposition du mélange à une radiation de 200 à 800 nm d'une source d'énergie radiante jusqu'à ce que la polymérisation ou réticulation du polymère bloc acrylique photoinféré et du monomère radicalairement polymérisable ait lieu pour former un article dentaire partiellement durci ;
- (iii) le façonnage de l'article dentaire de l'étape (ii) partiellement durci, selon la forme désirée ;
- 35 (iv) la répétition des étapes (ii) et (iii), si nécessaire, jusqu'à ce que la forme désirée de l'article dentaire, partiellement durci ait été obtenue ; et
- (v) l'exposition de l'article dentaire partiellement durci de l'étape (iii) ou (iv) à une exposition finale à une radiation de façon à obtenir l'article dentaire final durci.